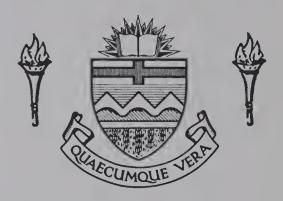
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	ETHANOLAMINE SOLUTIO	ONS
DEGREE FOR WHICH	THESIS WAS PRESENTED	M.Sc., Chemical
		Engineering
YEAR THIS DEGREE	GRANTED 1975	

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# SOLUBILITY OF CO<sub>2</sub> AND H<sub>2</sub>S IN ETHANOLAMINE SOLUTIONS

by



#### A THESIS

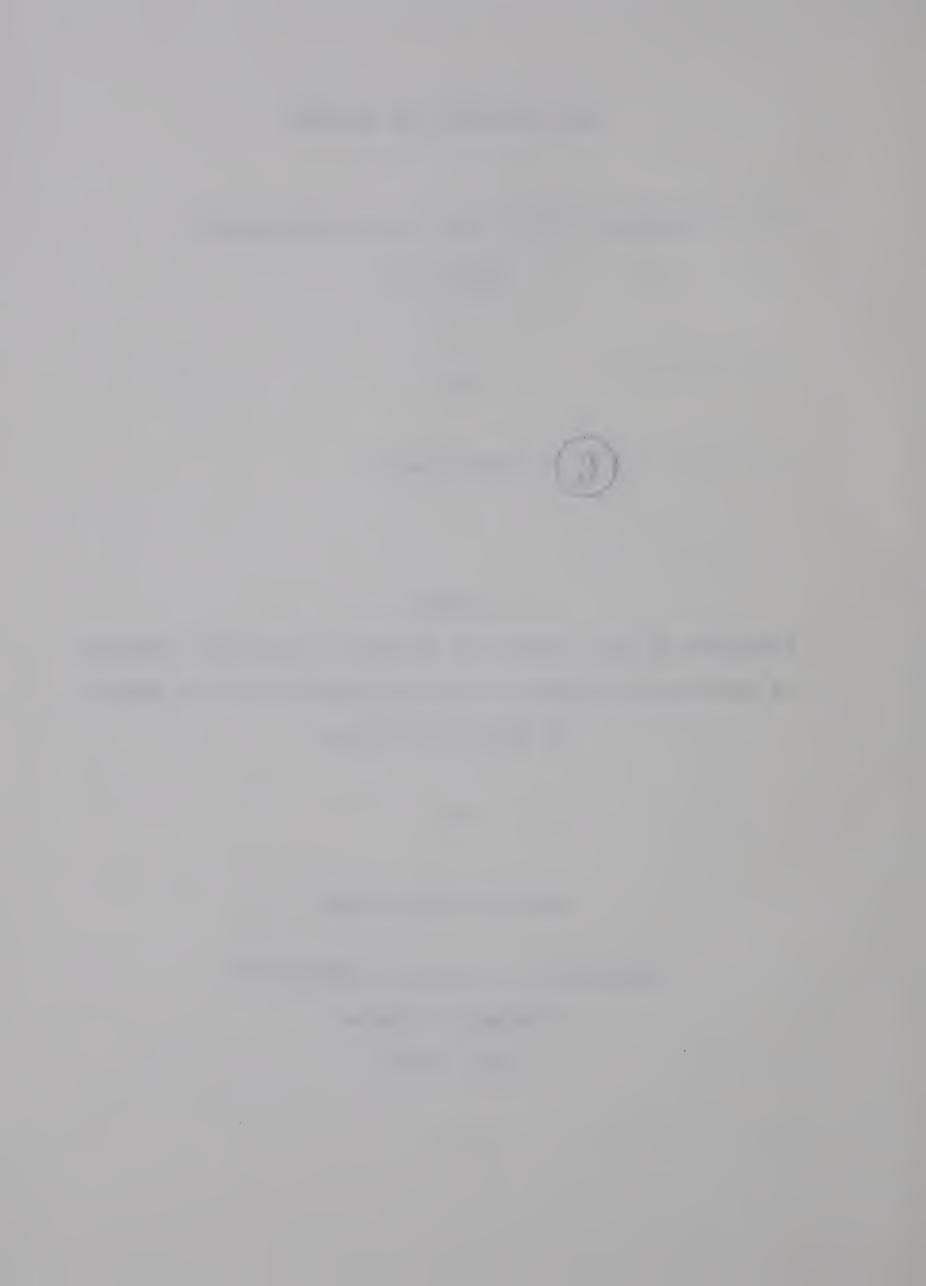
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING
EDMONTON, Alberta
FALL, 1975



#### THE UNIVERSITY OF ALBERTA

#### FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "SOLUBILITY OF CO<sub>2</sub> AND H<sub>2</sub>S IN ETHANOLAMINE SOLUTIONS", submitted by Pervaiz Nasir in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.



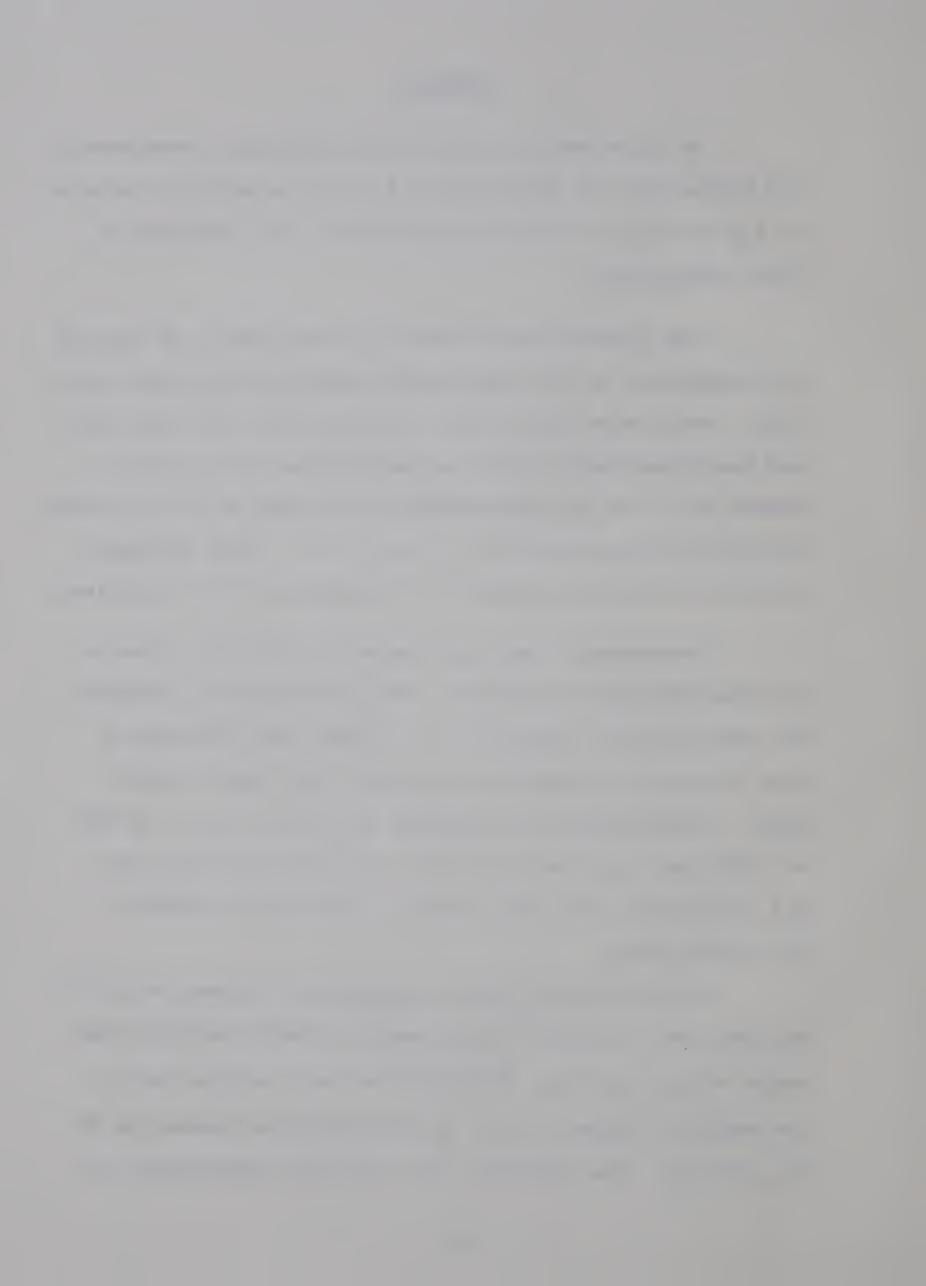
#### ABSTRACT

An experimental apparatus was designed, constructed and tested for the measurement of very low partial pressures of  ${\rm H_2S}$  and  ${\rm CO_2}$  in aqueous ethanolamine (EA) solutions at high temperatures.

The apparatus was tested by measurements of  ${\rm CO}_2$  and  ${\rm H}_2{\rm S}$  solubility in the region where previous data were available. Tests were carried out for  ${\rm CO}_2$  at 60°, 80° and 100°C and monoethanolamine (MEA) concentrations of 2.5 and 5.0 normal (N). For  ${\rm H}_2{\rm S}$  measurements were made at 80° and 100°C with MEA concentrations of 2.5 and 5.0 N. Good agreement with the literature proved the reliability of the apparatus.

Measurements were also made at conditions where no previous data were available. The 80° and 100°C isotherms, for both pure CO<sub>2</sub> and H<sub>2</sub>S in 2.5 N MEA, were extended to very low partial pressure of the acid gas (about 0.0001 psia). Measurements for mixtures of H<sub>2</sub>S and CO<sub>2</sub> in 5N MEA at 100°C were also made for very low loadings of CO<sub>2</sub> and H<sub>2</sub>S (each being less than about 0.1 mole/mole of MEA) in the liquid phase.

The theoretical models proposed by Klyamer et al.  $^{13}$  and Kent and Eisenberg  $^{10}$  were used to predict partial pressures of  ${\rm CO}_2$  and  ${\rm H}_2{\rm S}$ . Modifications were carried out in the model of Klyamer et al. by incorporating fugacities of  ${\rm CO}_2$  and  ${\rm H}_2{\rm S}$ . The functions, for activity coefficients of



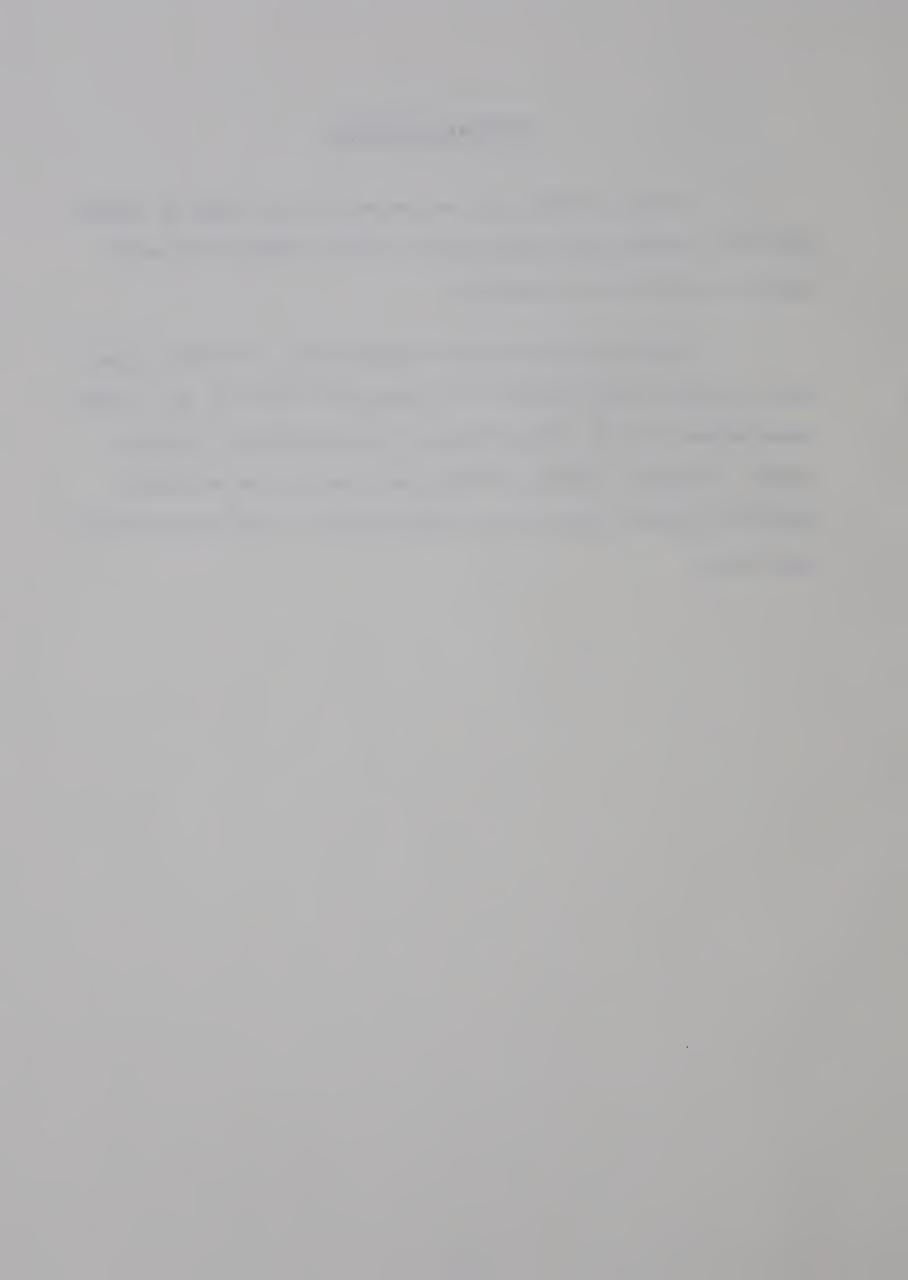
ions in the solution, were modified to include the effects of temperature and initial EA concentrations. Predictions from these three models (namely Klyamer et al., Kent and Eisenberg, and modified Klyamer et al.) were compared with the experimental data obtained in this work, as well as that from the literature. For most cases the Modified Klyamer et al. model gives the best fit of the experimental data. For the simple systems (i.e., aqueous EA solutions containing either CO<sub>2</sub> or H<sub>2</sub>S), however, the model of Kent and Eisenberg gives a slightly better fit of the experimental data.



#### ACKNOWLEDGEMENTS

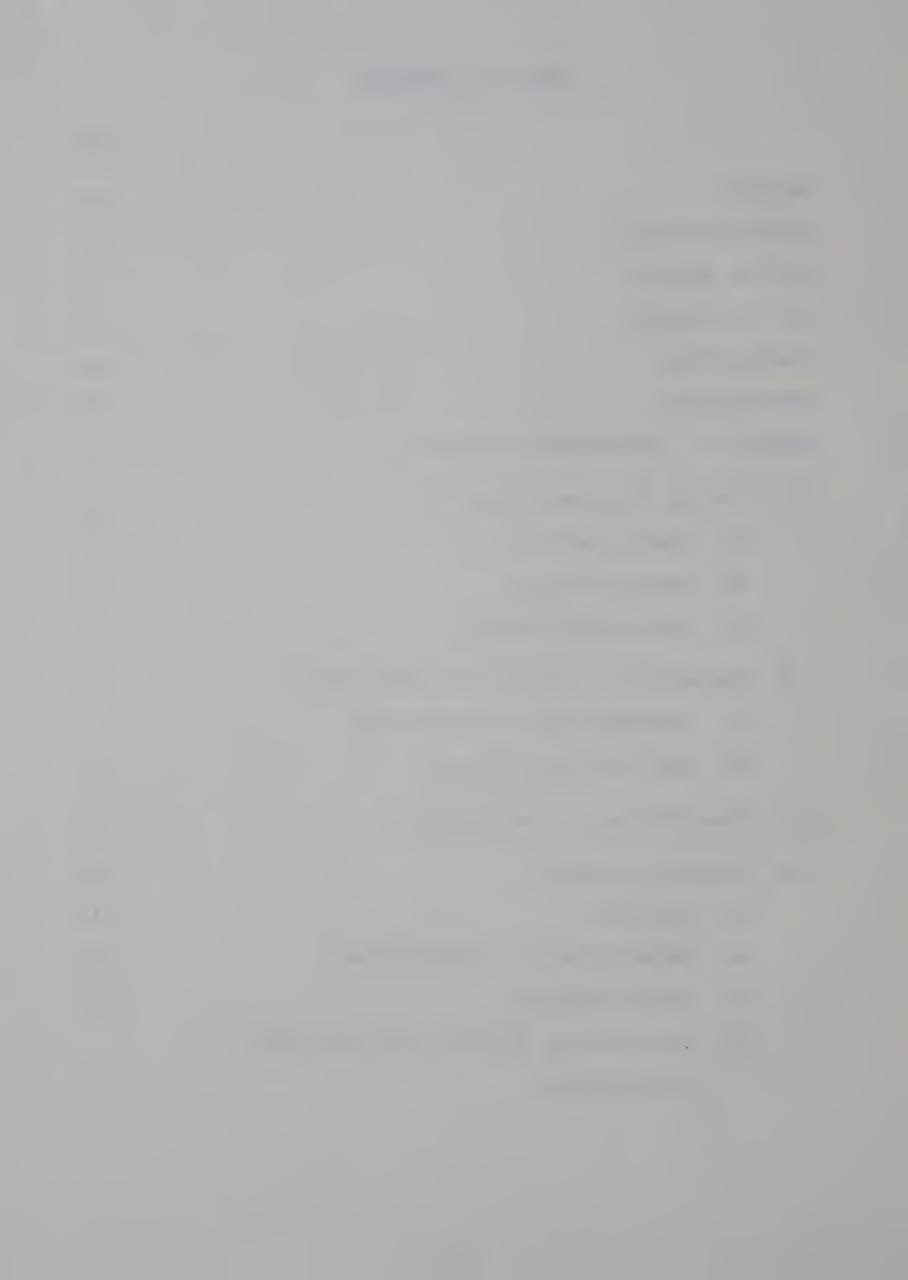
Sincere thanks are expressed to Dr. Alan E. Mather for his guidance and supervision without which this work would not have been possible.

Helpful criticism and suggestions of fellow graduate students and friends, in particular Jong Il Lee, Jamal Abou-Kassem and Dr. Eddy Isaacs, are gratefully acknowledged. Finally, special thanks are due to the workshop staff for their help in the fabrication of the experimental apparatus.

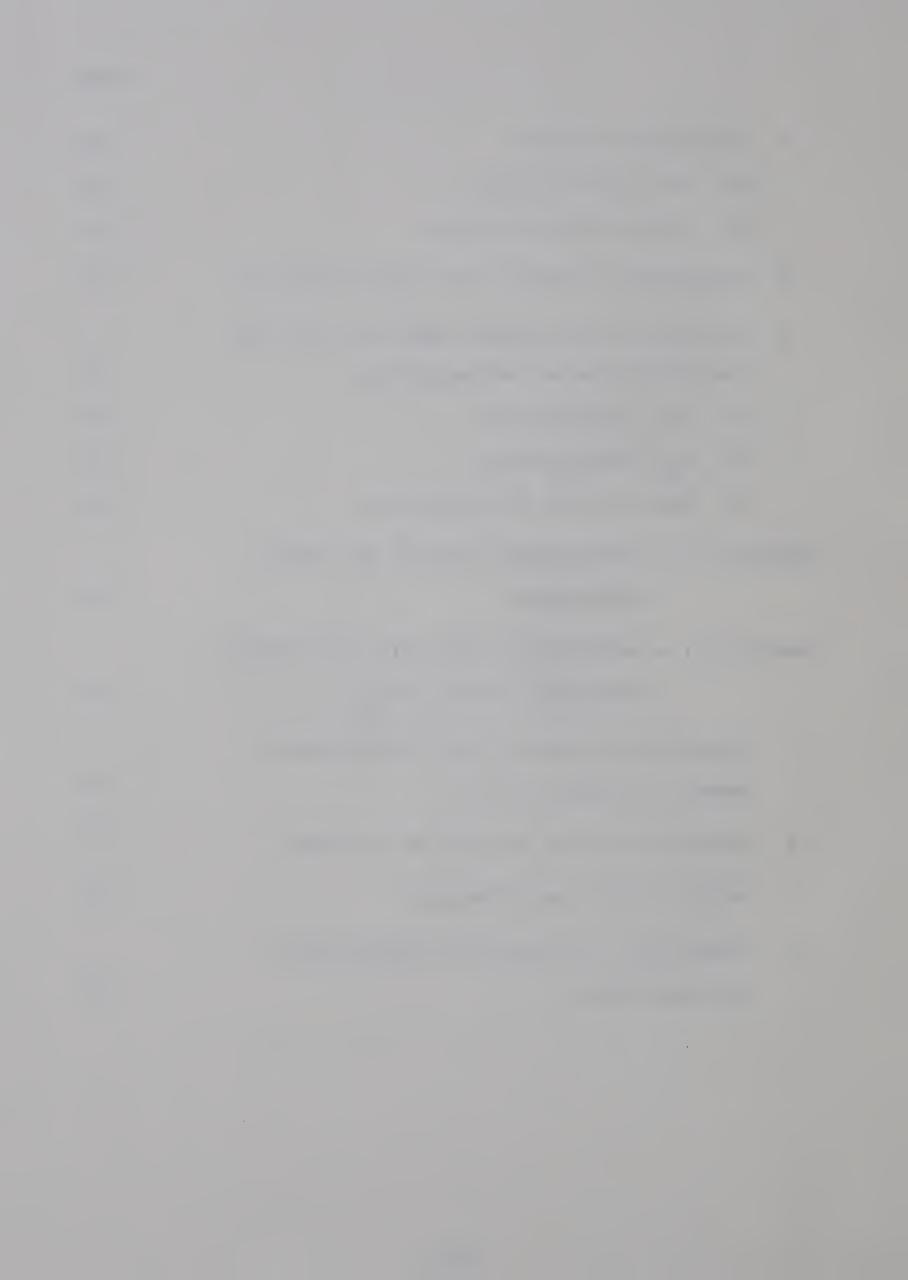


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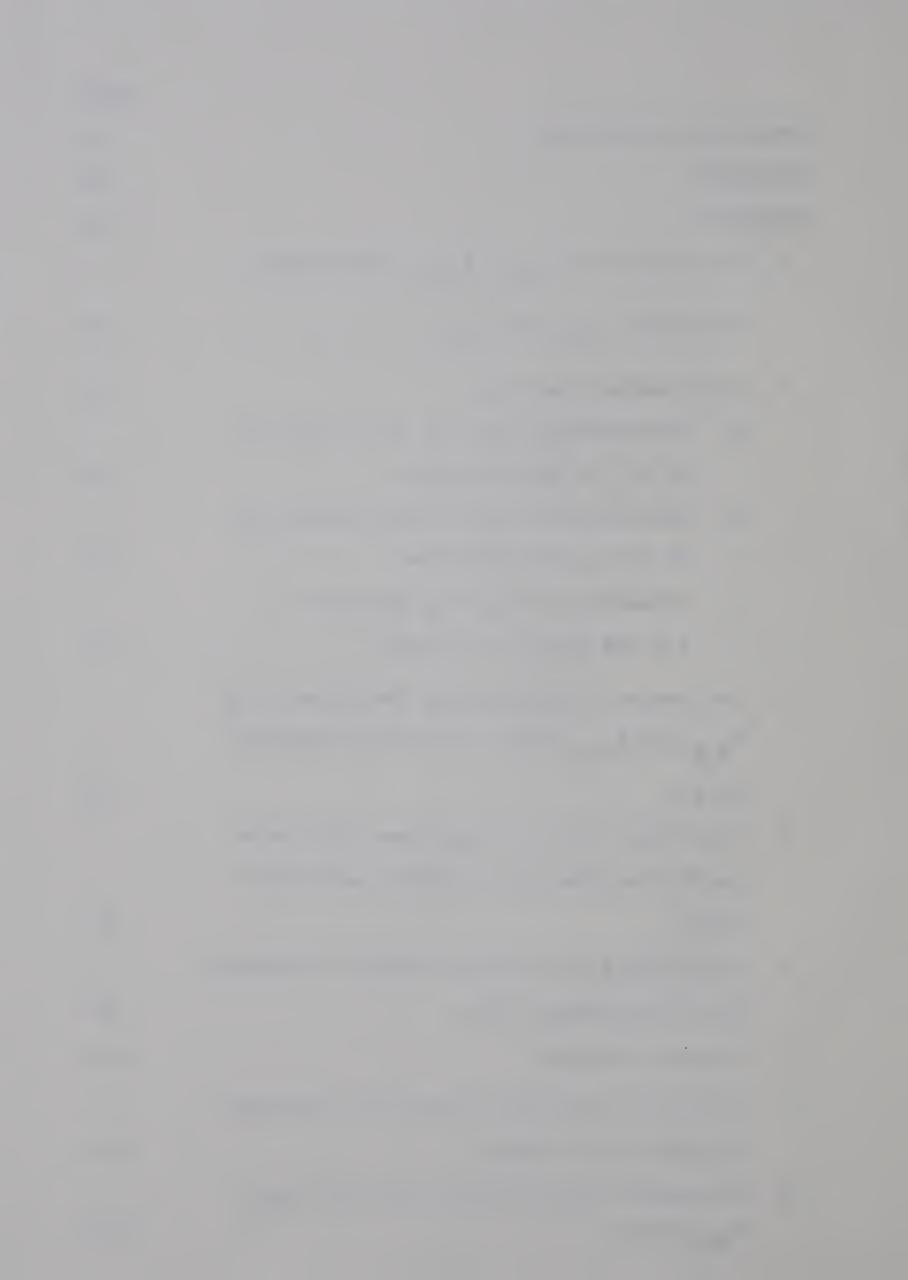
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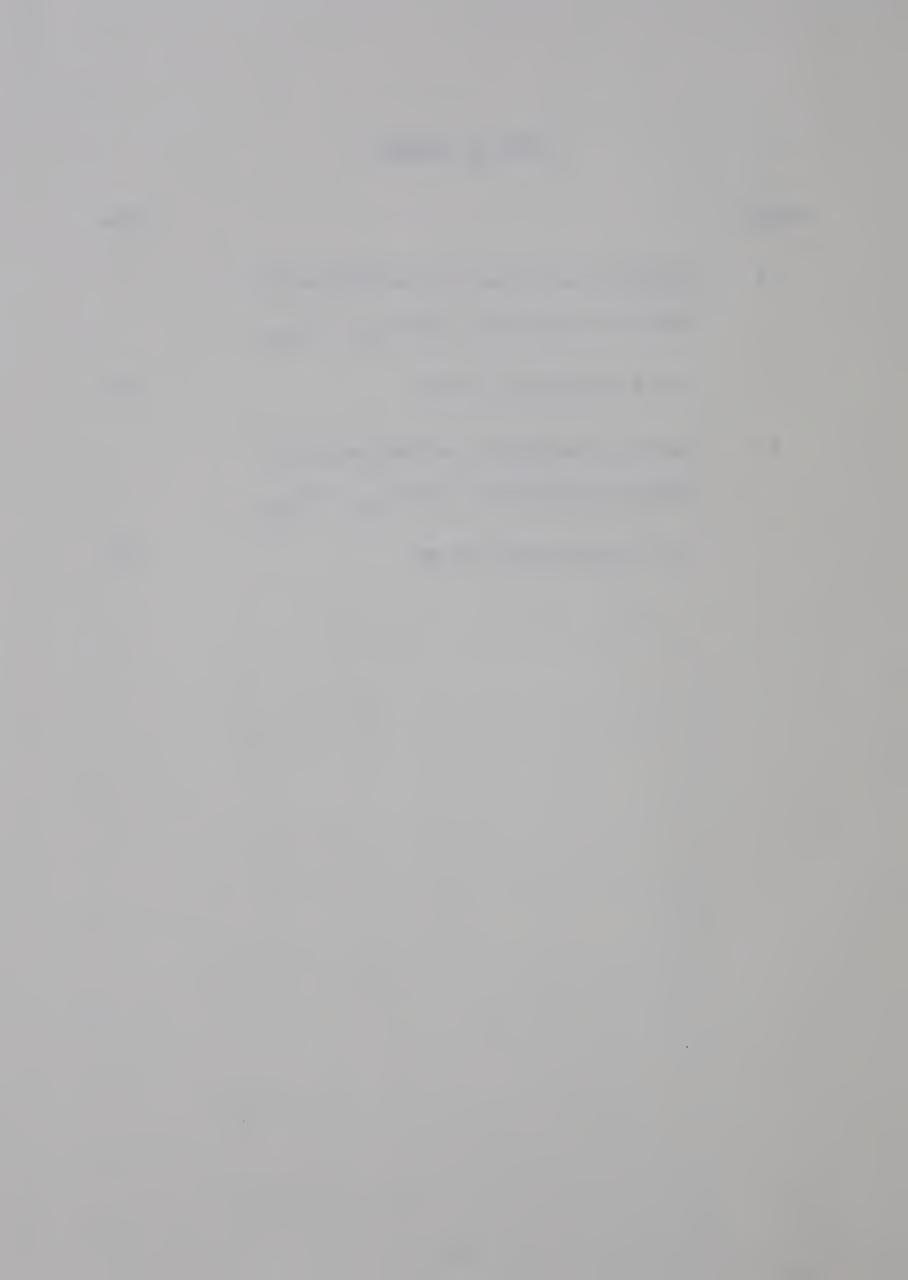


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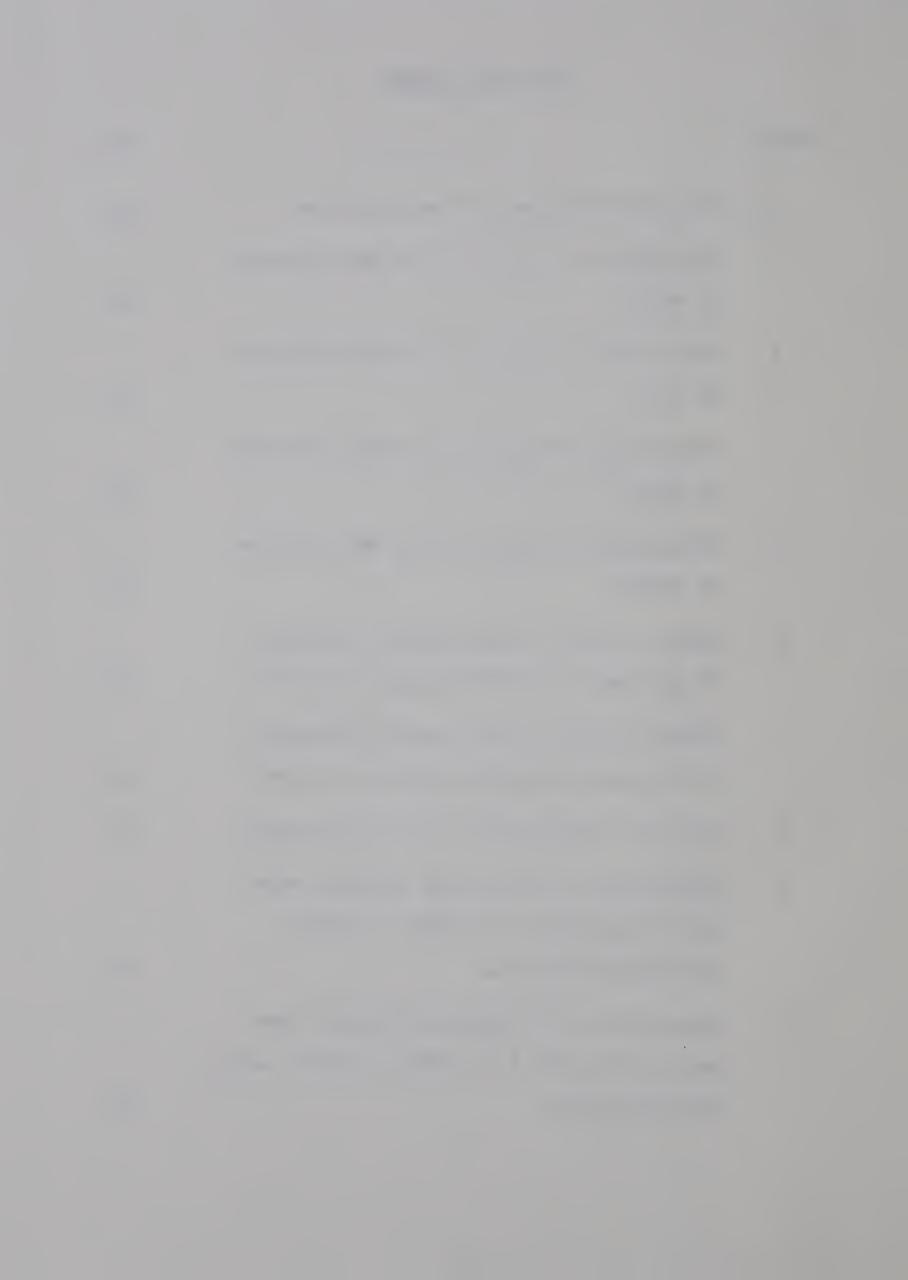


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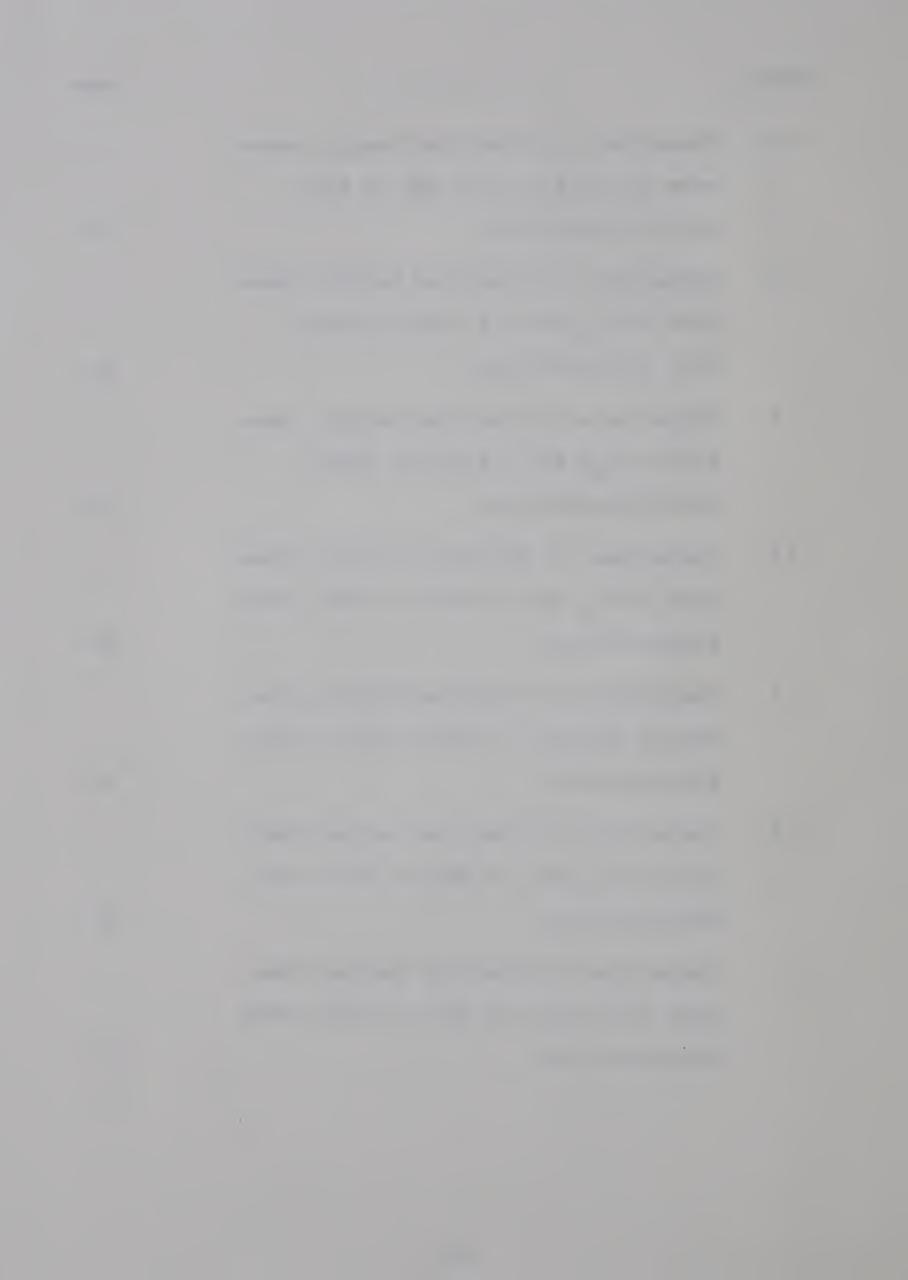


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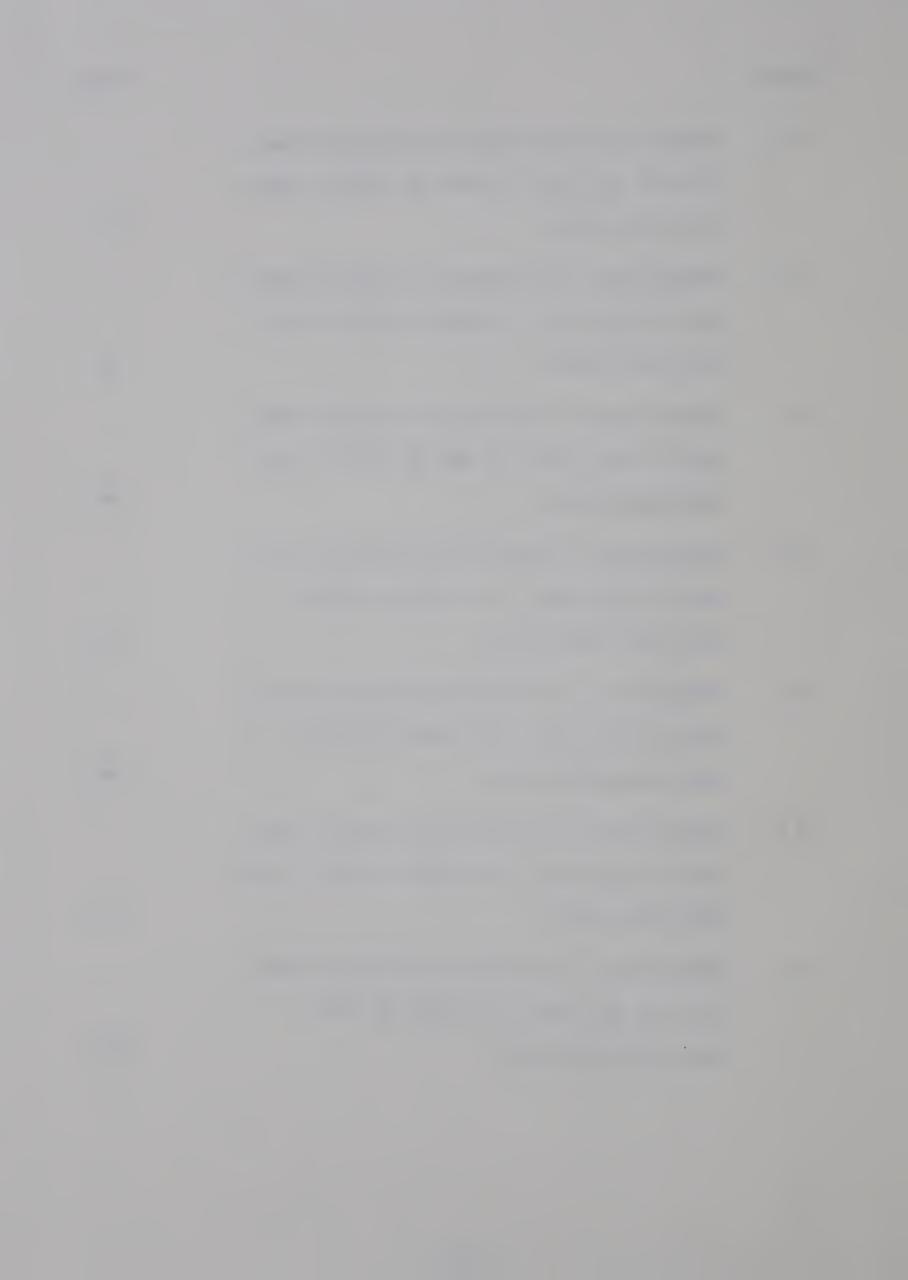
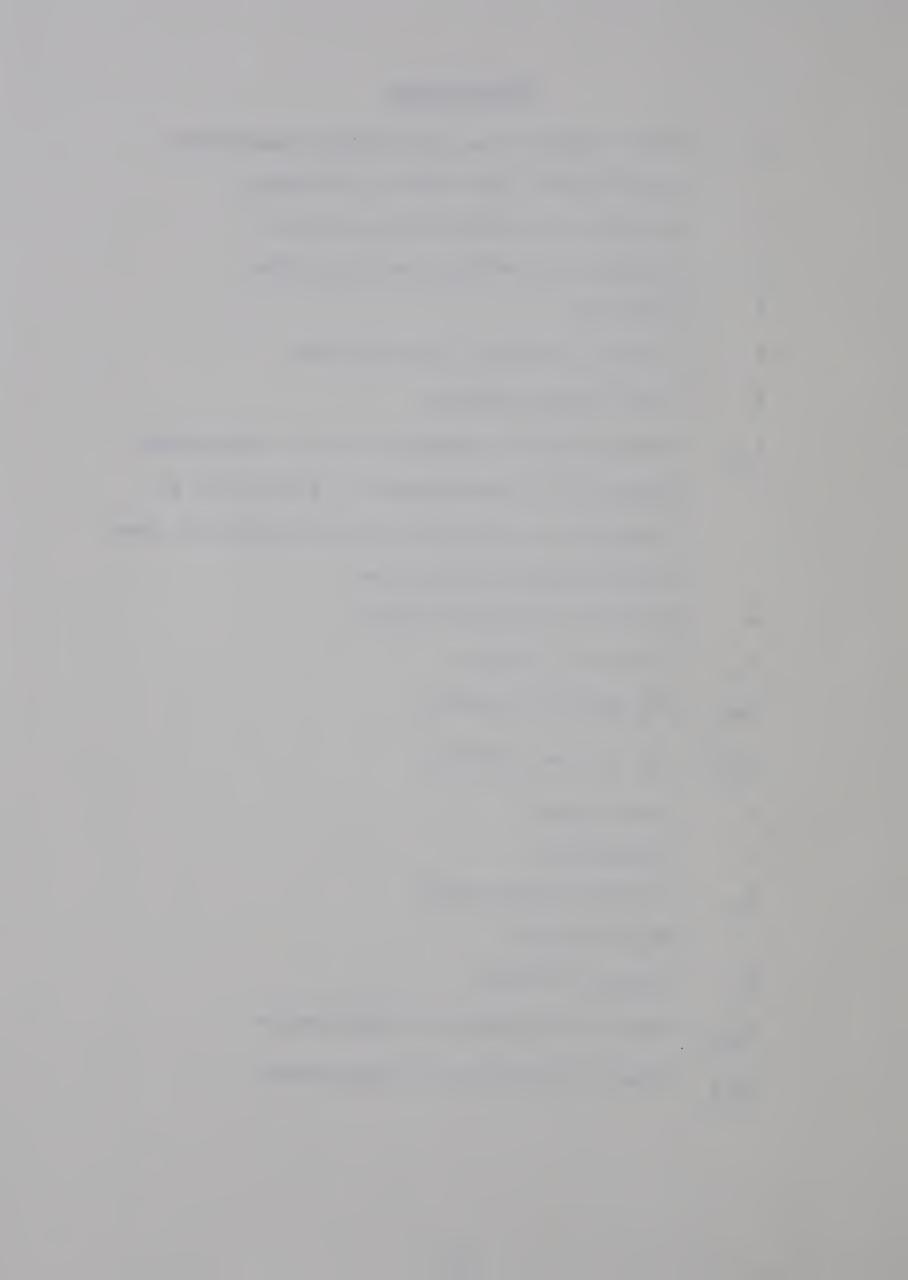


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## NOMENCLATURE

а	Ratio between the un-ionized ethanolamine
	activity and the activity of water
a	Constant in Redlich-Kwong equation
b	Constant in Redlich-Kwong equation
f	Fugacity
Н	Inverse of Henry's Law constant
K	Equilibrium constant
k <sub>ij</sub>	Characteristic constant for i-j interaction
m	Molality of ethanolamine in Klyamer et al.
·	correlation; molarity of ethanolamine in Kent
	and Eisenberg correlation
N	Normality of ethanolamine
Pc	Critical pressure
Pco <sub>2</sub>	CO <sub>2</sub> partial pressure
P <sub>H2</sub> S	H <sub>2</sub> S partial pressure
R	Gas constant
т	Temperature
Tc	Critical temperature
v	Molar volume
V <sub>C</sub>	Critical volume
X <sub>CO2</sub>	Moles of CO <sub>2</sub> /mole of ethanolamine
x <sub>CO2</sub>	Moles of H <sub>2</sub> S.mole of ethanolamine



Y<sub>i</sub> Mole fraction of component i

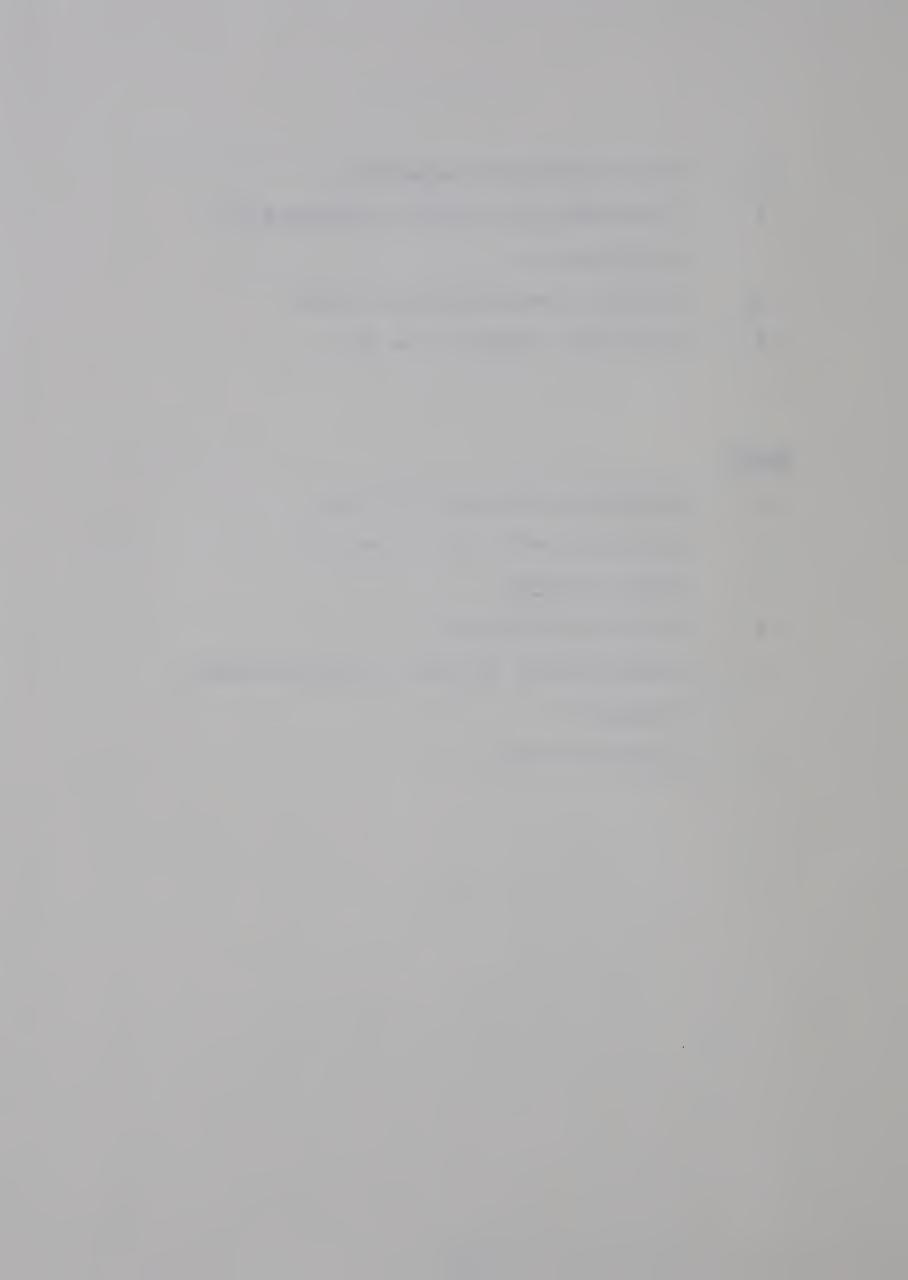
z Compressibility factor; carbamate ion concentration

z<sub>c</sub> Critical compressibility factor

z<sub>i</sub> Electrical charge on an ion

# $\frac{\text{Greek}}{\alpha}$ $\alpha$ Activity coefficient of water $\gamma$ Activity coefficient of an ion $\mu$ Ionic strength $\phi$ Fugacity coefficient $\Omega$ Dimensionless constant in Redlich-Kwong equation

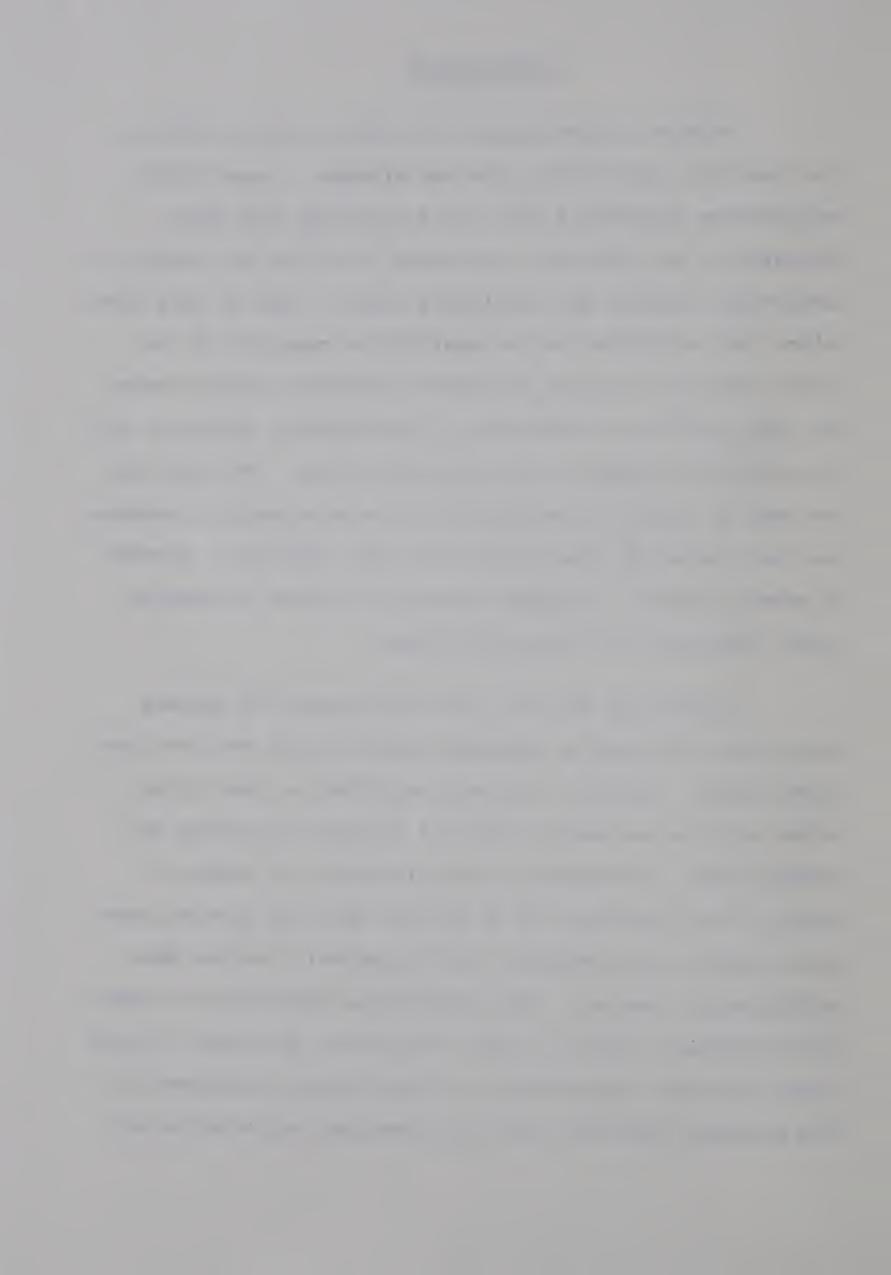
Acentric factor



### INTRODUCTION

Aqueous ethanolamines are widely used in industry for removing H<sub>2</sub>S and CO<sub>2</sub> from gas streams. Vapor-liquid equilibrium solubility data for H<sub>2</sub>S and CO<sub>2</sub> and their mixtures in EA solutions are needed to aid in the design of amine-type natural gas sweetening units. Data of this type allow the estimation of the equilibrium capacity of the amine solution for each different sweetening system design for the particular conditions of temperature, pressure, and concentration found in the processing units. The data may be used to check the feasibility of more economical designs not yet tested by plant experience and, therefore, provide a means to guide a program intended to reduce sweetening plant investment and operating costs.

Solubility data for acid gas-aqueous EA systems have been collected by numerous investigators over the last forty years. However, the data published to date do not cover all the necessary ranges of solution strengths and temperatures. The region of low loadings, in terms of moles of acid gas/mole of EA and low acid gas partial pressure (where most commercial units operate), has not been sufficiently covered. This project was undertaken to cover this important region of very low partial pressures of acid gases and high temperatures. To make these measurements a low pressure apparatus had to be designed and constructed.



To be able to use this apparatus with confidence for regions where no data exist, some measurements had to be made to reproduce existing data.

While the equilibrium solubility data are useful in themselves, it is desirable to have a computer-oriented correlation which reproduces the experimental results, and which can be extrapolated outside the range of the data with some degree of confidence. So far only two solubility models have been proposed for CO2-H2S-water-EA systems by Klyamer et al. 13 and Kent and Eisenberg 10. The starting point for both of these models is the postulation of chemical reactions occuring in the aqueous EA solution containing the acid gases. The model of Klyamer et al. uses activity coefficients, for ions in the solution, to account for the non-ideality of the liquid phase. Kent and Eisenberg have incorporated all the non-idealities in two empirical They determined these parameters from experiparameters. mental data. Neither of these models is reliable over all conditions of solution strengths and temperatures. Modifications in the Klyamer et al. model (made in this work) improved substantially, the reliability of prediction of equilibrium partial pressures from a knowledge of liquid composition and temperature.

In Chapter I, design considerations, construction, and operating details of the experimental apparatus are



described. In Chapter II, comparison of the experimental data with those of literature is presented in graphical form, along with the data obtained in this work for regions where no previous data are available. Chapter III, discusses the theoretical models for prediction of equilibrium partial pressures of  ${\rm CO_2}$  and  ${\rm H_2S}$  when other conditions are known. This is followed by comparison of the models.



### CHAPTER I

### EXPERIMENTAL METHOD

In this chapter the design considerations, construction and operation of the experimental apparatus used in this work will be described.

# A. Design Considerations:

Basically three different methods have been employed for vapor liquid equilibrium studies of Hydrogen Sulphide - Carbon Dioxide - Water - Ethanolamine systems:

- (a) Static Method
- (b) Dynamic Method
- (c) Circulation Method

### a) Static Method:

In this method a closed cell containing the amine solution with a certain concentration of acid gas (or gases) is used. A motor and gear train usually constitutes the rocking mechanism. The whole assembly is immersed in an oil or air bath. This method has been used by Reed and Wood<sup>28</sup> for measurement of CO<sub>2</sub> partial pressures ranging from 1.5 to 1.7 atm; Jones et.al<sup>9</sup> from 0.56 to 7000 mm of mercury; Goldman and Leibush<sup>8</sup> from 10 to 2000 mm of mercury; Lee, Otto and Mather<sup>15,16</sup> for partial pressures of CO<sub>2</sub>



between 0.1 psia and 827 psia and partial pressures of  ${\rm H}_2{\rm S}$  between 0.1 psia and 306 psia.

# b) Dynamic Method:

Either a gas blend of  $N_2$ ,  $CO_2$  and  $H_2S$  or pure  $N_2$  is passed through a number of saturators containing amine solution with a certain concentration of acid gases. The gas phase is repeatedly analyzed after a certain time interval, until two or three similar readings indicate that equilibrium has been reached. This method is called the 'Dynamic Method'.

Mason and Dodge <sup>25</sup> used this method to measure CO<sub>2</sub> partial pressures ranging from 0.19 to 14.9 psia. Leibush and Shneerson <sup>23</sup> used it for H<sub>2</sub>S partial pressure measurements when the partial pressures were less than 6.7 psia; also for measuring solubilities of mixtures of CO<sub>2</sub> and H<sub>2</sub>S when partial pressures of CO<sub>2</sub> plus H<sub>2</sub>S were less than 3 psia. This method was also used by Atwood et al. when partial pressure of H<sub>2</sub>S was between 0.0005 to 5720 mm of mercury. Lyudkovskaya and Leibush <sup>24</sup> used it for CO<sub>2</sub> partial pressure measurements in the range of 36.8 psia to 588 psia: Riegger, Tartar and Lingafelter <sup>29</sup> employed this method for measurement of H<sub>2</sub>S partial pressure in the range of 25 to 700 mm of mercury. Muhlbauer and Monaghan <sup>26</sup> also used dynamic method for acid gas solubility studies at 25°C.

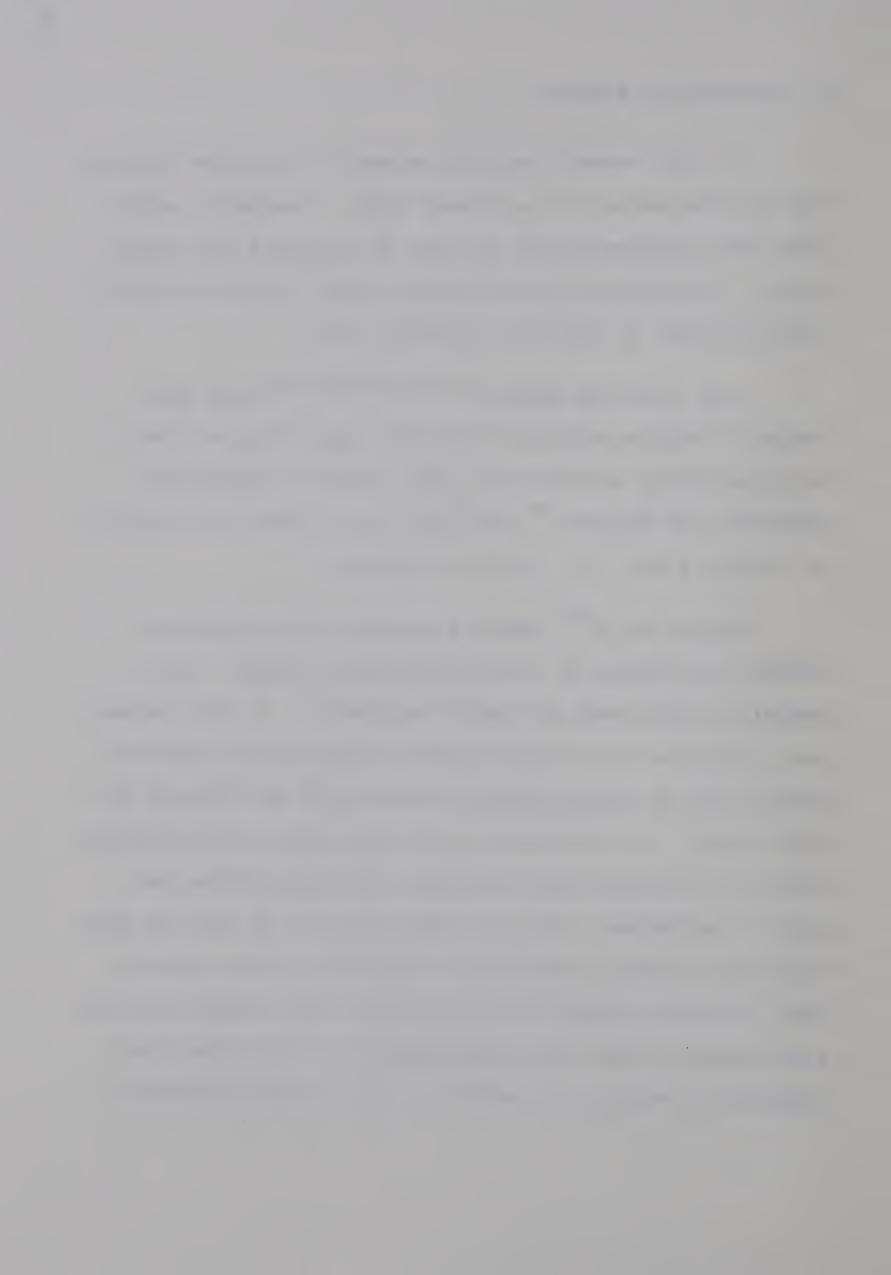


### c) Circulation Method:

In this method the vapor phase is circulated through the equilibrium cell in a closed loop. A magnetic pump or some other pumping device is used to circulate this vapor phase. To analyze the vapor phase a small part of the circulating vapor is bled to a sampling cell.

Lee, Otto and Mather <sup>17,18,19,20,21,22</sup> used this method to obtain solubility data for H<sub>2</sub>S or CO<sub>2</sub> or their mixtures in MEA or DEA over a wide range of conditions. Muhlbauer and Monaghan <sup>26</sup> also used this method for pressures ranging from 1 to 1000 mm of mercury.

Murzin et al.<sup>27</sup> combined dynamic and circulation methods and termed it 'Flow-Circulating' method. This method is often used in kinetic studies<sup>31</sup>. In this method gas circulates in a closed system and equilibrium between phases sets in during multiple bubbling of gas through the fluid layer. In the meantime, the gas flow is continuously forced in a closed cycle and equal flow equilibrium gas phase is withdrawn. The gas flow forced in as well as that withdrawn is only a small part (up to 5%) of the overall flow, therefore supply of pure gas into the system does not substantially alter the equilibrium and at the same time sampling of sufficient quantity of gas is made possible.

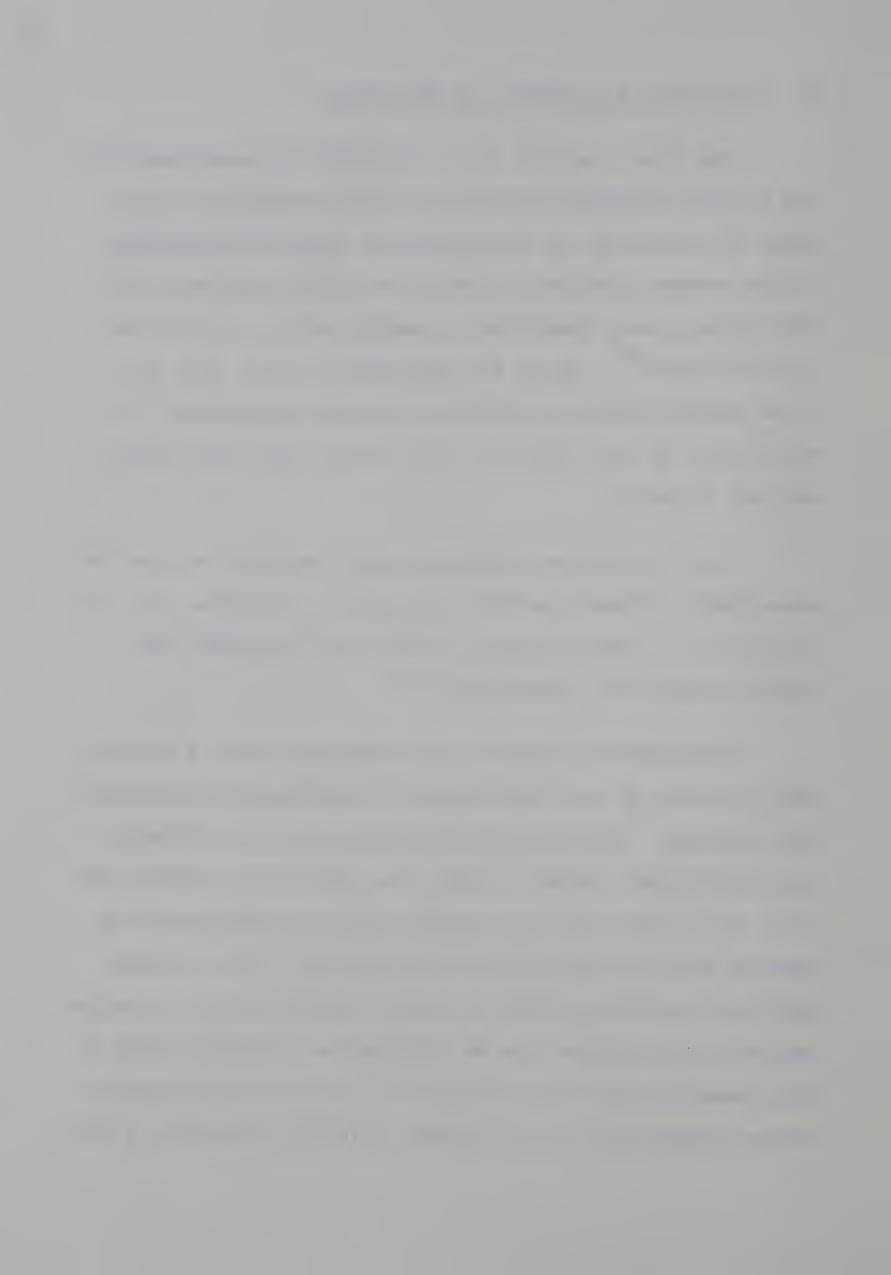


# B. Selection of a Method for This Work:

The static method is not suitable for measurement of low partial pressures because the large sampling of gas phase for analysis can substantially disturb equilibrium in the system. Besides at very low partial pressures of acid gases a very long time is needed before equilibrium is established <sup>27</sup>. Since the apparatus in this work had to be used for very low partial pressure measurement (of acid gases) it was obvious at the outset that this method was not reliable.

The circulation method was also rejected because for measurement of small partial pressures it requires the circulation of a large quantity of gas and this makes the method excessively cumbersome <sup>26,27</sup>.

ient quantity of the vapor phase is continuously available for analysis. Thus gas phase analysis in no way affects the equilibrium. Also, if the flow rate of the carrier gas (e.g. N<sub>2</sub> in this case) is chosen carefully equilibrium is reached within a reasonable time interval. This method has the disadvantage that at higher temperatures, the amine concentration changes due to evaporation of water unless a high gauge pressure is maintained. But the amine concentration changes can be controlled to within reasonable limits



by a slightly higher absolute pressure than the partial pressure of water plus amine at that temperature and by maintaining a low flow rate of  $N_2$  through the saturators.

Two alternate routes are available in the dynamic method itself:

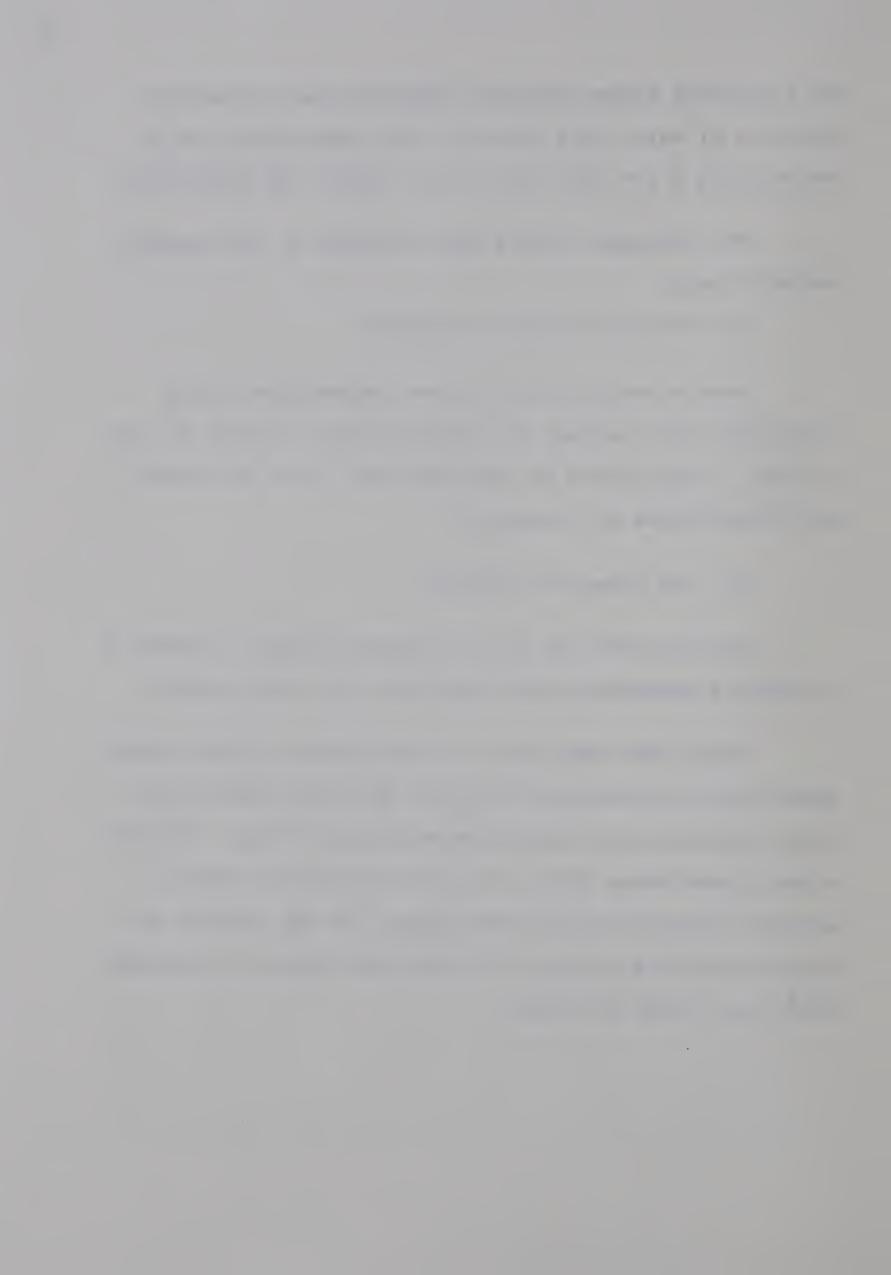
a) Solution Saturation Method:

Here a carrier gas of known composition viz. N<sub>2</sub> containing acid gas(es) is passed through a series of saturators. Equilibrium is indicated when inlet and outlet gas compositions are identical.

### b) Gas Saturation Method:

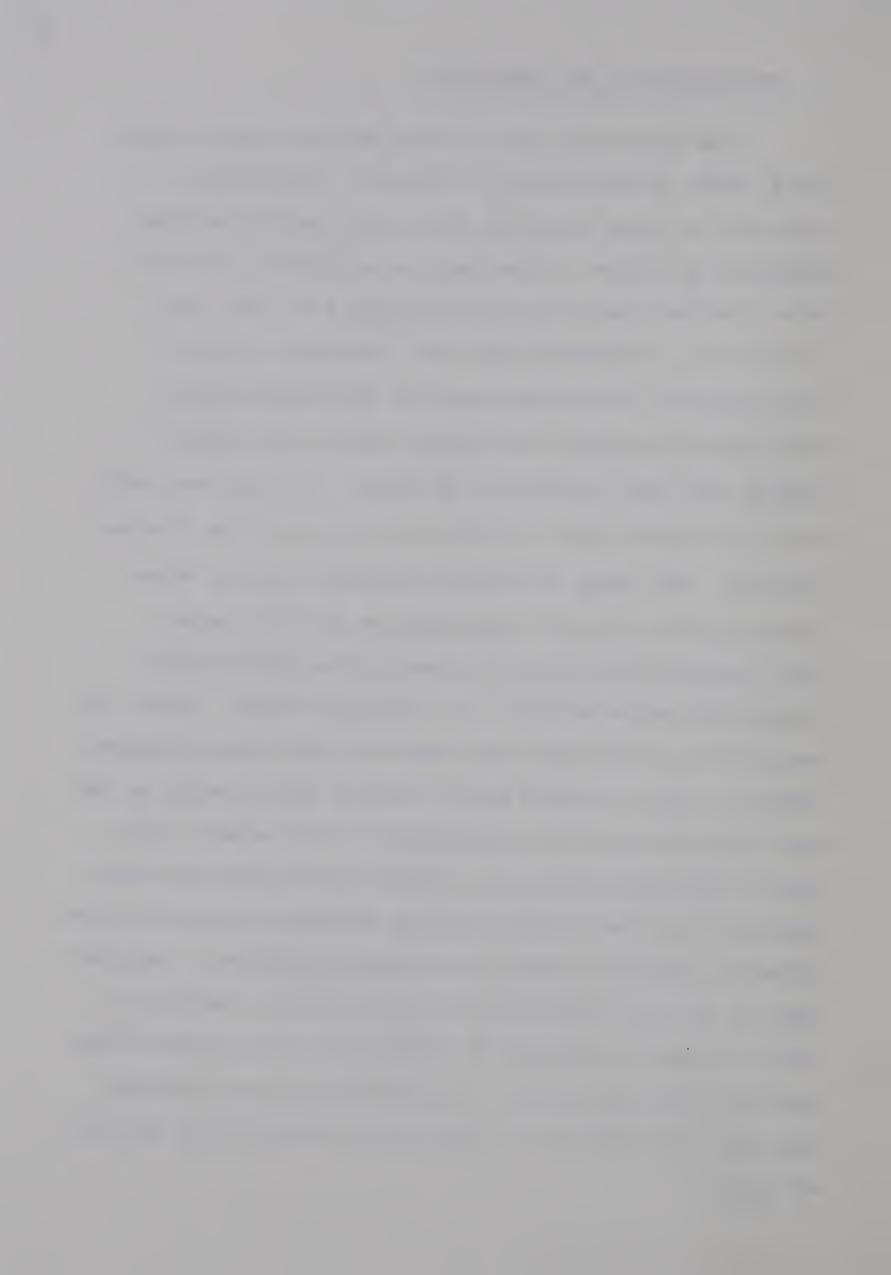
Pure carrier gas (N<sub>2</sub>) is passed through a number of saturators containing amine solution with acid gas(es),

Since this work had to be carried out in the region where partial pressures of  ${\rm CO_2}$  and  ${\rm H_2S}$  were always less than 1 psia the gas saturation method was chosen. The obvious reason being that it is not practical to have a uniform concentration of acid gas(es) in the carrier gas when the partial pressure of these acid gases is extremely low 1 (e.g. below 0.1 psia).



# C. Description of the Apparatus:

The apparatus used for this work was quite simple and is shown schematically in Figure 1. Basically it consisted of three identical 250 ml gas washing bottles connected in series. These bottles were kept in an oil bath. Carrier gas (N2) passed through a 25 foot long, 0.25 in. O.D. stainless steel coil immersed in the oil along with most connections and all the three bottles. After passing through the heating coil N<sub>2</sub> was bubbled through the three saturators in series. N<sub>2</sub> flow was regulated by a needle valve to make sure that the flow rate was The three saturators contained aqueous amine solution with a certain concentration of acid gas(es). This solution was prepared by passing the acid gas(es) through the amine solution in a separate bottle. After the saturators N<sub>2</sub> saturated with water and acid gas(es) passed through a trap to remove water droplets before going to the gas chromatograph (GC), and finally to the exhaust line. The gas continuously passed through the GC sampling loops; therefore gas phase monitoring was possible at whatever time intervals desired, without disturbing the system. The pressure in the final saturator was indicated by a mercury or water manometer depending on whether high or low gauge pressure was being maintained. Liquid samples were withdrawn from the last bottle by a back-forcing method to be described later.



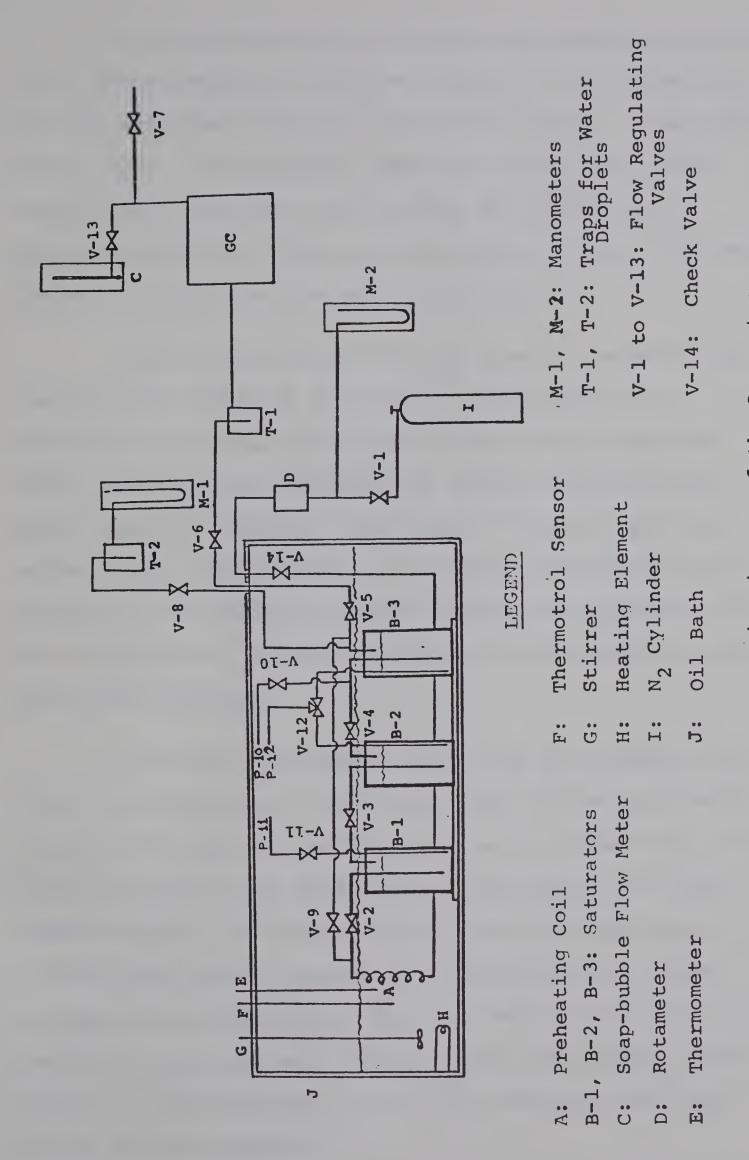


Figure 1 - Schematic Diagram of the Apparatus



All interconnecting lines were of seamless stainless steel tubing except at inlet and outlet of the gas washing bottles which had glass ball and socket joints. Glass and metal were connected by Kovar-to-borosilicate glass seals. Only stainless steel valves and connections were used because of the corrosive nature of the acid gases (especially H<sub>2</sub>S) and the amine solutions.

Glass tubing fused from the side of the bottle and reaching the bottom of the bottle (from inside) was used for filling and discharging of the amine solutions. These lines, too, were connected by Kovar-to-borosilicate glass seals to stainless steel tubing through a ball and socket joint. The operation of filling, discharging and cleaning of the bottles without removing the apparatus from the oil-bath will be described later in the section on experimental procedure.

The traps used before the GC and the manometer to remove condensed water drops were simply 250 ml erlenmeyer flasks with a side arm which served as an outlet line. The inlet stainless steel tubing passed through an air tight rubber stopper. The outlet lines from the traps were of polyethylene plastic because the vapor phase had cooled to near room temperature. The trap near the manometer was used to prevent any vapor from reaching the column of mercury if a leak developed in the line connecting the last bottle to the manometer.



flow rate through the system, a rotameter was used before the carrier gas entered the saturators. A similar rotameter was initially used before the gas entered the GC, but this had to be replaced by a soap-bubble flow meter, because of the moist nature of the gas which caused the indicator to stick in place at low flow rates. A flow meter is desirable after the GC because in the event of a leak in the apparatus the two flow meters (one before the saturators and the other after them) would give different flow rates. The soap-bubble flow meter (after the GC) was found to be adequate. The only disadvantage in using a soap-bubble flow meter was that it sometimes affected the pressure in the system since the line to the exhaust had to be closed to divert flow through the bubble-meter.

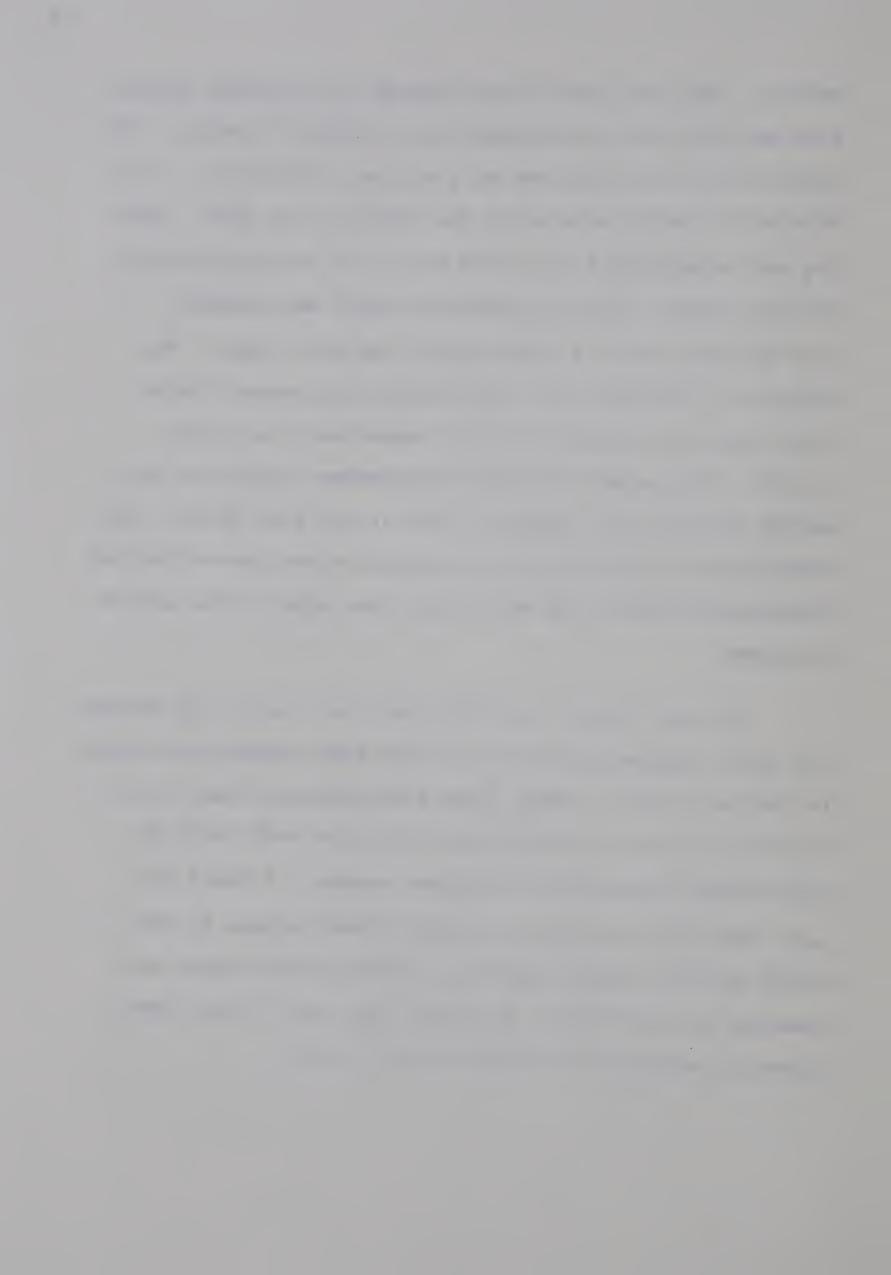
The saturators were mounted on a stainless steel platform with a heating coil surrounding them on supports from the platform. This assembly was immersed in oil but all the valves were above the oil surface and could be reached easily. Filling-discharging lines and the liquid sampling lines could also be reached conveniently.

The bath consisted of a 3 foot x 2 foot x 1.5 foot rectangular stainless steel container containing about 40 gallons of Grade-30 motor (mineral) oil as the heating



medium. The outer walls were covered by styrofoam insulation and the bath was enclosed in a hardboard casing. Agitation of oil was obtained by a stirrer rotated by a 0.25 HP electric motor mounted on the cover of the bath. Heating was accomplished by a 1500 watt, 220 volt cylindrical heating element (General Electric) which was screwed into the bath about 4 inches above the bath floor. The heater was connected to a Hallikainen Instrument Thermotrol, which controlled the bath temperature to within ±0.01°C. The sensor from the temperature controller was passed into the oil through a hole in the bath cover. The temperature of the bath was indicated by two pre-calibrated thermometers, one in the middle and the other at the end of the cover.

The gas inlet, gas outlet and the line to the mercury (or water) manometer came out of the bath through two holes in the bath cover. These lines had stainless steel quick-connects so that the apparatus inside the bath could be disconnected conveniently whenever needed. A small lid just above the saturator-assembly allowed access to the valves and for liquid sampling, filling, discharging and cleaning of saturators. At other times the lid was kept closed to minimize the escape of oil vapors.



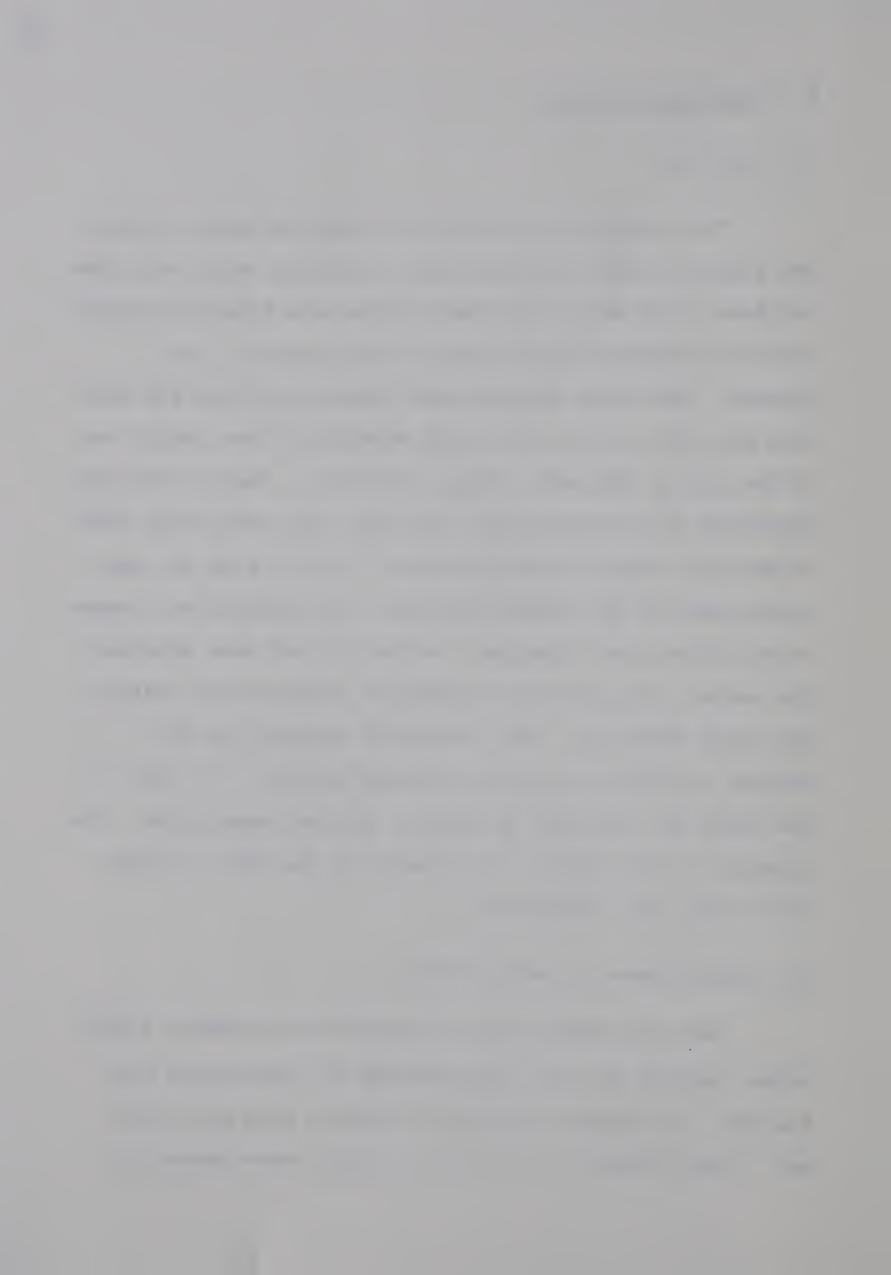
# D. Operating Details:

### a) Start-Up:

The bottles were filled with desired amine solution and lowered on the stainless steel platform which held them in place. The ball and socket joints were properly greased (with Dow Corning high vacuum silicone grease) clamped. The whole assembly was lowered into the oil bath with only the inlet, outlet and manometer lines coming out of the top of the bath through two holes. These lines were connected to the manometer, inlet gas line and outlet line to the GC, through quick-connects. At this time all the valves were in the closed position. The stirrer was turned on and after some turbulence in the oil had been obtained, the heater along with the thermotrol (temperature controller) were turned on. The thermotrol reading was set through a calibration curve obtained earlier. It took a few hours for the bath to reach a desired temperature. example, it took about 6 to 7 hours for the bath to reach 100°C from room temperature.

# b) Establishment of equilibrium:

Once the temperature of the bath had reached a steady value, carrier gas  $(N_2)$  flow through the saturators was started. A nitrogen pressure of about 5 psig was first set. Then valves 1, 2, 3, 4, 5, 6 and 7 were opened in



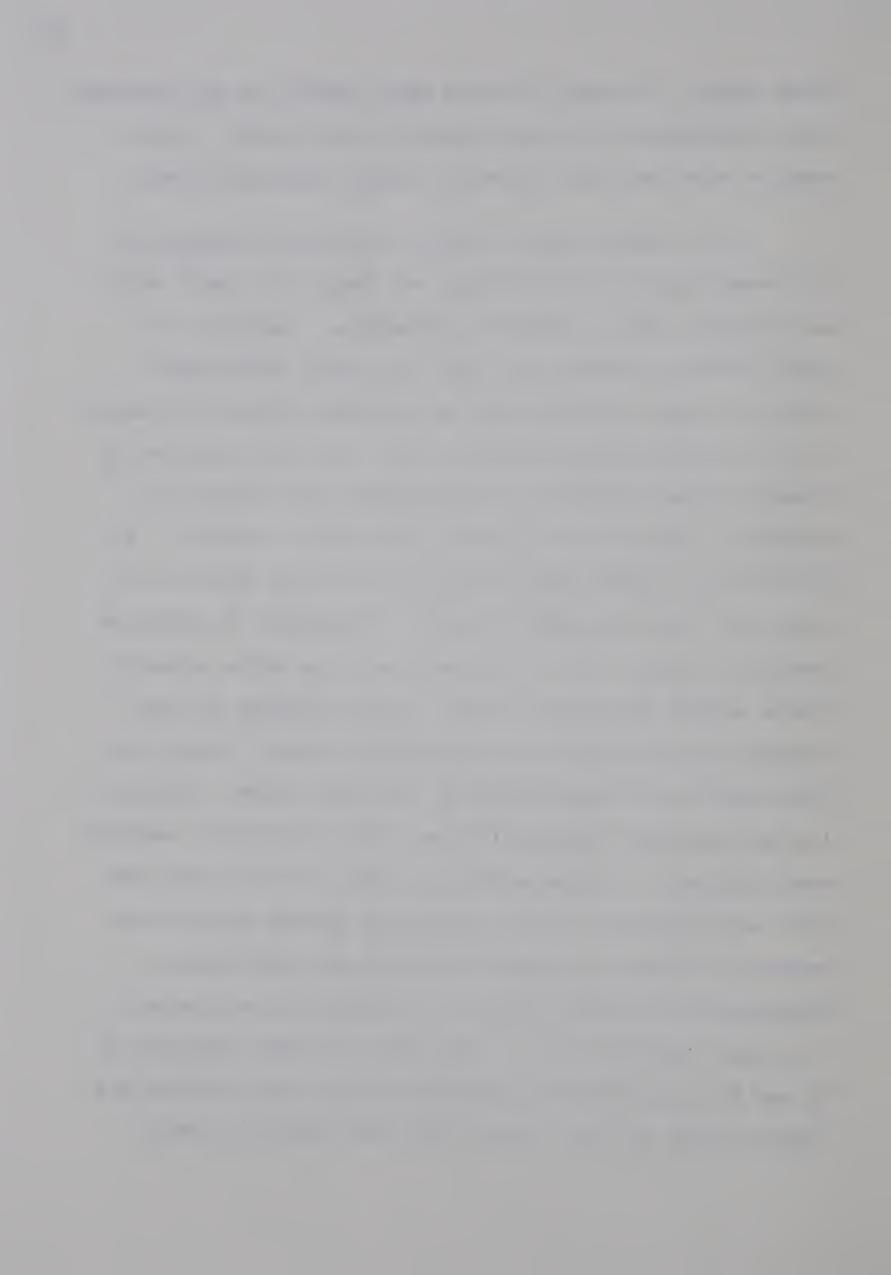
that order. A small change in mercury level in the manometer, M-2, showed that gas had started flowing through the system. Also the rotameter showed flow of N<sub>2</sub> through the system. Now valve-13 was opened and then valve-7 closed, to measure the flow rate of carrier gas through the saturators by the soap-bubble meter. If the flow rate was above 15 ml/min valve-1 was closed slightly until the rate reached about this value. The final flow rate setting was obtained by the fine-metering valve-6. A N<sub>2</sub> flow rate of about 10 ml/min was found to be the optimum. Once the desired flow rate had been obtained valve-7 was opened again and valve-13 closed. Valve-8 was now opened to connect the last saturator, B-3, to the manometer, M-1, which gave the gauge pressure in B-3.

For temperatures up to 80°C, N<sub>2</sub> flow through the amine solution did not affect the amine concentration much because the partial pressure of 2.5 normal aqueous MEA solution is about 2.8 psia<sup>7</sup> at 60°C and 6.6 psia<sup>7</sup> at 80°C. About 4 hours were allowed for the N<sub>2</sub> to flow through the saturators. After that the gas composition was monitored every half-hour using the GC. The gauge pressure from M-1 was also noted each time. When two identical GC analysis had been obtained and M-1 readings were also almost the same, equilibrium had been established. To make sure one hour more was allowed and M-1 and GC readings



taken again. If these readings were similar to the previous ones establishment of equilibrium was confirmed. Liquid samples were now taken using the method described later.

For a temperature of 100°C the partial pressure of 2.5 normal aqueous MEA solution was about 13.7 psia which was slightly above atmospheric pressure. Therefore to avoid excessive removal of water and hence appreciable change in amine concentration an absolute pressure of about 15 to 16 psia was maintained in B-3. This was achieved by closing valve-5 slightly in combination with valve-6 to maintain a flow rate of carrier gas around 10 ml/min. the case of 5 normal MEA solution the partial pressure of water plus MEA was about 13 psia . Therefore, an absolute pressure of about 14.5 to 15 psia kept the amine normality change within desirable limits. No was allowed to flow through the saturators at 10 ml/min for about 3 hours before starting the monitoring of the vapor phase. Monitoring was continued every half hour until consistent readings were obtained. A close watch was kept on M-1 to make sure that gauge pressure did not vary much between monitorings because a change in pressure disturbs the equilibrium. Micrometering valve-6 was used to maintain this pressure to a near constant value. Once two consistent readings of GC and M-1 were obtained, equilibrium had been reached and liquid sample was now taken. The time needed to reach



equilibrium depends on the acid gas concentration in the liquid phase. For higher concentrations it usually took about 4 to 5 hours if the gauge pressure in B-3 was maintained around a certain value. For lower acid gas concentrations a little longer time was usually needed.

# c) Liquid sampling:

Once the GC analysis of the vapor phase had shown that equilibrium had been reached and also a reading of the manometer, M-1, had been taken, it was time for obtaining a representative sample of the liquid phase. Saturator B-3 was the one with which the gas phase was in contact last and hence the liquid sample was withdrawn from B-3. To do this valves 2, 4, 5 and 8 were closed. Valve-9 was now opened to apply a slight back pressure on the liquid in B-3. Valve-10 was now opened. Liquid was forced through the fritted glass end in B-3 through valve-10 and into a liquid sampling bottle at port, p-10. The first 5 to 10 ml of the sample were discarded since they had flushed the line and contained some drops from the previous sample. After this flushing about 10 ml were collected in a liquid sampling bottle which was then stoppered and allowed to cool to room temperature before chemical analysis.

# d) Discharging, Cleaning and Refilling of Saturators:

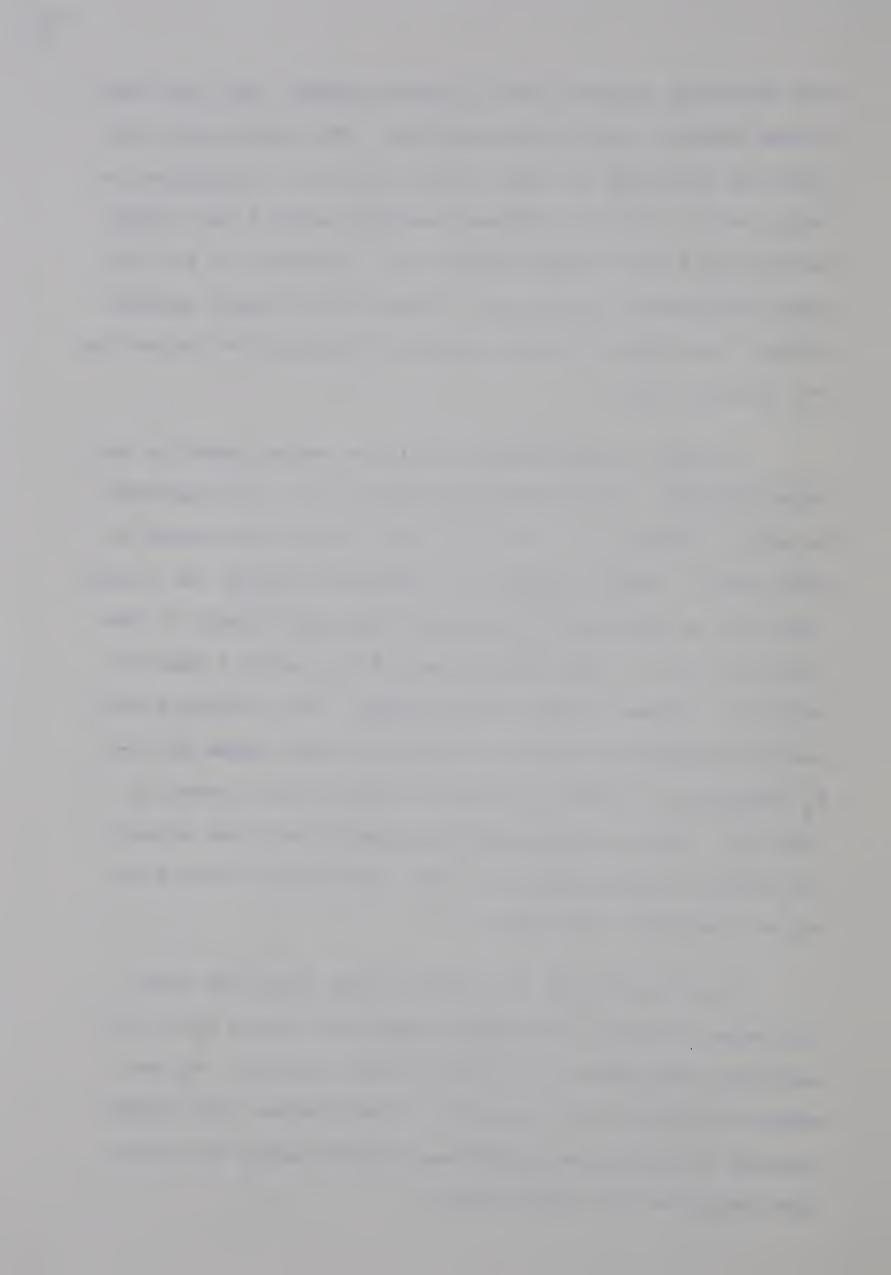
To discharge amine solution the bottles were emptied in the order: B-3, B-2 and finally B-1. Valve-9 and then



the three-way valve-12 for B-3 were opened. All the other valves except 1 were closed earlier. The discharged solution was collected in the *filling-bottle* or a container at port, p-12. Once B-3 had been emptied valve-4 was opened and valve-12 was turned towards B-2. Contents of B-2 were again collected at port p-12. After B-2 had been emptied valves 3 and then 11 were opened to discharge the contents of B-1 at port, p-11.

Filling of the bottles could be accomplished in any order desired. To fill B-1, a filling-bottle was connected to p-11. Valves 11, 3, 4, 5, 6 and 7 were then opened in this order. Amine solution (or cleaning liquid) was forced into B-1 by applying N<sub>2</sub> pressure above the liquid in the filling-bottle. Once B-1 had been filled with a desired solution, valves 11 and 3 were closed. The filling-bottle was now connected to p-12 and valve-12 was opened for B-2. N<sub>2</sub> pressure on liquid, in the filling-bottle, forced it into B-2. After B-2 had been charged valve-4 was closed and valve-12 opened for B-3. B-3 was filled in the same way as the other two bottles.

For cleaning of the bottles warm distilled water (or amine solution) was pushed into each bottle using the technique described for filling of the bottles.  $N_2$  was bubbled through this liquid for a few minutes (for proper rinsing) and then the liquid was removed using the procedure described for discharging.



Note that when the saturator assembly was at a high temperature (above 80°C) cleaning liquid or new amine solution was warmed before charging to prevent cracking (or breaking) of the glass due to sudden contraction.

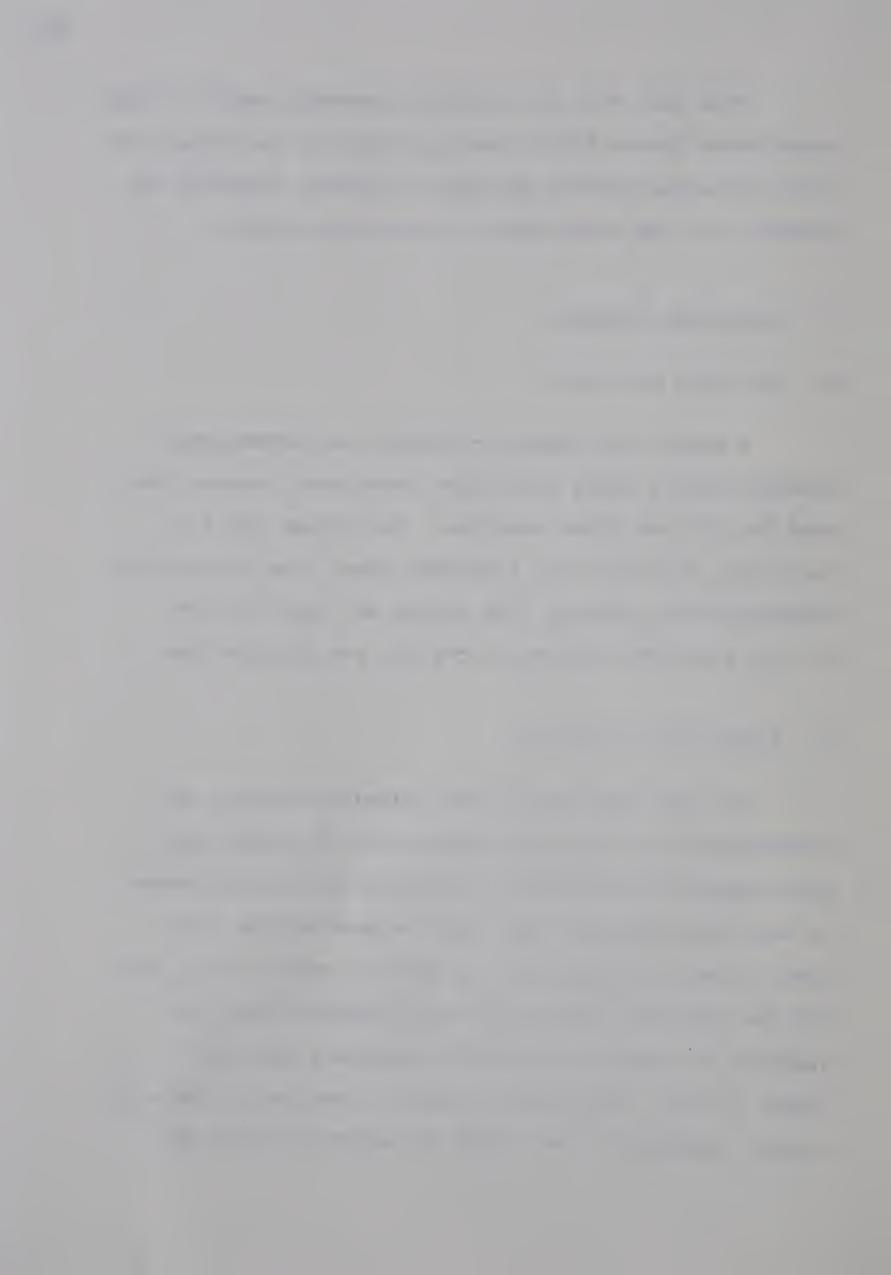
#### E. Analytical Methods:

# a) Gas Phase Analysis:

A model 5710A Hewlett-Packard gas chromatograph equipped with a Model 1750A disc integrator recorder was used for all gas phase analyses. The column was a 10 foot long, 0.25 in. O.D. stainless steel tube filled with CHROMOSORB-104 packing. The column was kept at 130°C for H<sub>2</sub>S and 110°C for CO<sub>2</sub> or for CO<sub>2</sub> and H<sub>2</sub>S mixtures.

### b) Liquid Phase Analysis:

In this work both direct titration methods and methods which rely on the evolution of CO<sub>2</sub> and/or H<sub>2</sub>S were tested for the chemical analysis of the acid gases. It was found that for very small concentrations (less than 0.1 mole acid gas(es) per mole of amine) of CO<sub>2</sub> and H<sub>2</sub>S the evolution methods are not reliable since the quantity of sample available for analysis was small (about 10 ml). Also almost always a fraction of the acid gas(es) remained in the liquid no matter how much the



technique was refined. A brief description of the analysis methods tried follows:-

#### Method-1:

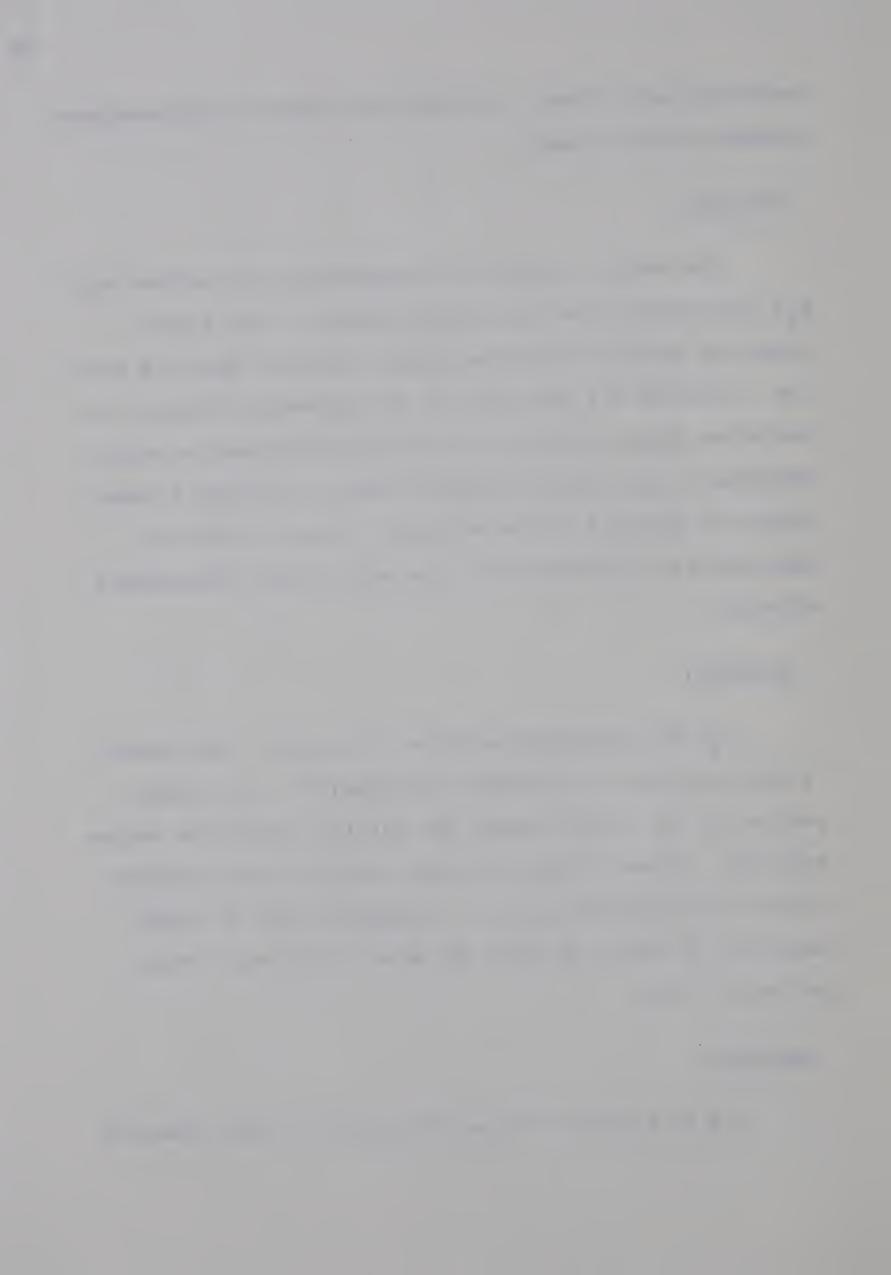
Dow Method; Iodometric Determination of evolved H<sub>2</sub>S: H<sub>2</sub>S was evolved from an aliquot portion of the liquid sample by addition of concentrated sulphuric acid and boiling. Purified air was drawn in by aspiration through the evolution flask carrying the evolved H<sub>2</sub>S through a reflux condenser, then through a gas scrubber containing a known volume of standard iodine solution. Excess iodine was determined by titration with standard sodium thiosulphate solution.

## Method-2:

H<sub>2</sub>S by Iodine-Thiosulphate Titration:- The method is that outlined by Kolthoff and Sandell<sup>14</sup>. An aliquot portion of the liquid sample was put into acidified iodine solution. Excess iodine was back titrated using standard sodium thiosulphate solution. Sulphuric acid in iodine should be at least 18 moles per mole of DEA or 11 moles per mole of MEA.

## Method-3:

H<sub>2</sub>S by Arsenite-Iodine Titration<sup>2</sup>:- Here Arsenious



sulphide was precipitated by H<sub>2</sub>S and the excess arsenite was back titrated using iodine solution. The reaction for this precipitation is:

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

The problem with this method was that a large volume (about 20 ml) of sample was needed for reliable results. With about 2 to 3 ml liquid samples reproducible results were not obtained.

#### Method-4:

H<sub>2</sub>S by direct I<sub>2</sub> titration: An aliquot of sample was titrated directly with 0.1 normal standard iodine solution in a medium buffered with sodium bicarbonate.

# Method-5:

Dow method for  ${\rm CO_2}^6$ :  ${\rm CO_2}$  was evolved from an aliquot portion of the sample by addition of concentrated sulphuric acid and heating. Evolved  ${\rm CO_2}$  was carried through a reflux condenser by purified air drawn in through an aspirator and then absorbed in a known volume of 0.1 N Barium Hydroxide  $({\rm Ba\,(OH)_2})$ . The excess  ${\rm Ba\,(OH)_2}$  was determined by titration with 0.1 normal hydrochloric acid to the phenolphthalein end point. Again the problem with this method was that to use up a reasonable amount of  ${\rm Ba\,(OH)_2}$  a large amount of liquid sample was needed,



especially for very low concentrations of CO<sub>2</sub>. Since a large liquid sample was not feasible, this method was discarded.

#### Method-6:

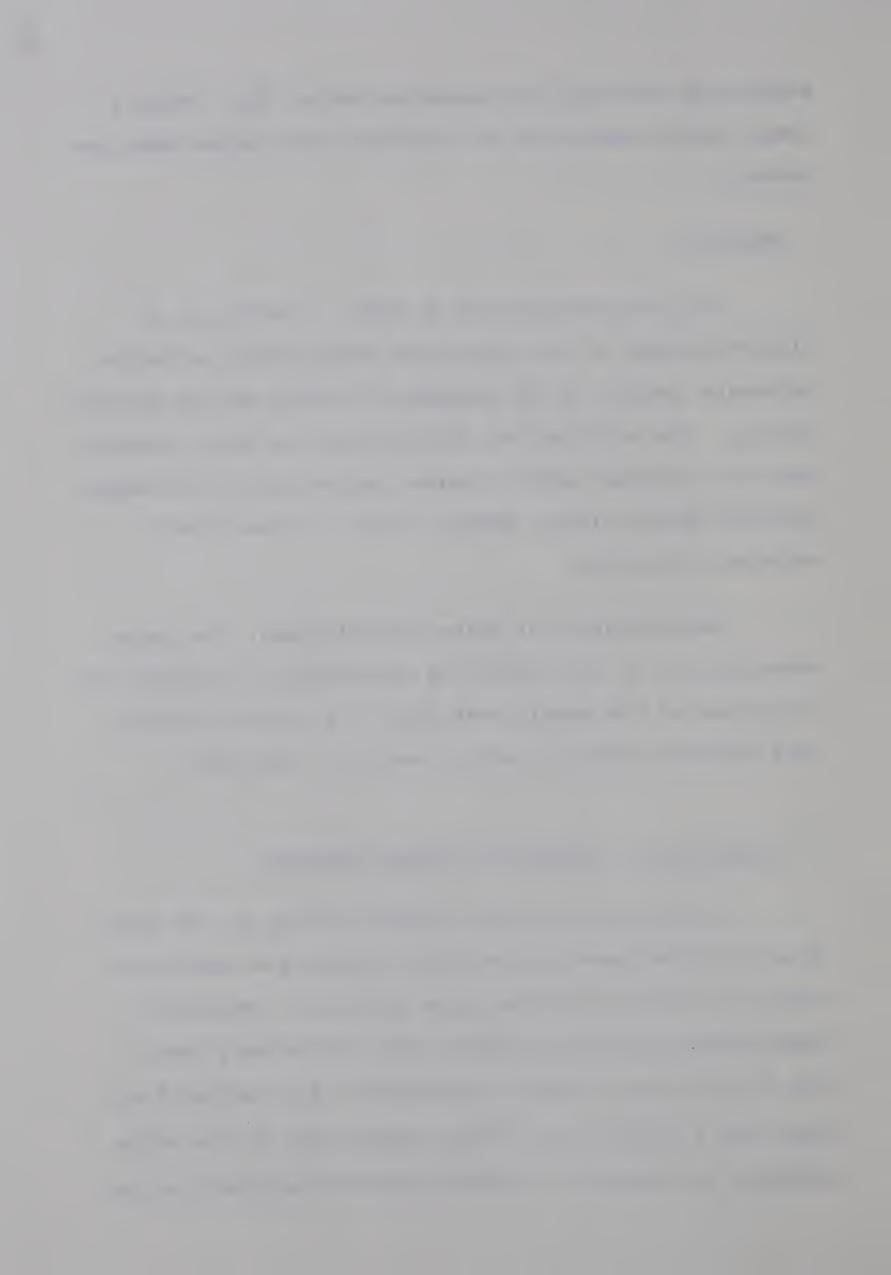
CO<sub>2</sub> by precipitation as BaCO<sub>3</sub>: The CO<sub>2</sub> in an aliquot portion of the sample was precipitated as Barium Carbonate (BaCO<sub>3</sub>) in the presence of excess Barium Chloride (BaCl<sub>2</sub>). The solution was filtered and the BaCO<sub>3</sub> precipitate was titrated with 0.1 normal hydrochloric acid using modified methyl orange (Methyl Orange - Xylene Cyanol solution) indicator.

Determination of Amine Concentration: The amine concentration in the liquid was determined by titration of an aliquot of the sample with about 0.1 normal sulphuric acid solution employing methyl red as an indicator.

# F. Selection of Methods for Liquid Analysis:

As mentioned earlier methods relying on evolution of acid gas(es) were not reliable at very low concentrations of acid gases in the amine solution. Therefore, these methods were not pursued after preliminary tests.

Out of the direct titration methods for H<sub>2</sub>S, Method-4 always gave a larger value of H<sub>2</sub>S composition in the amine solution as compared to iodine-sodium-thiosulphate method



(Method-2). Data in the literature were reproduced within reasonable limits using the iodine-thiosulphate method, while with Method-4 the H<sub>2</sub>S partial pressure was always lower for the determined H<sub>2</sub>S composition using this method. This indicated that liquid phase H<sub>2</sub>S determination was incorrect in the positive direction i.e., Method-4 always gave a higher H<sub>2</sub>S composition than actual. Later it was found that this was due to the fact that some iodine was used up by thiosulphate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) present in a sample. If the amount of iodine used up by thiosulphate was determined and then subtracted from the total, the iodine consumed by H2S was obtained. This gave results which were nearly identical to those given by iodine-thiosulphate (Method-2) method. Since reliability of iodine-thiosulphate titration has been confirmed before 14 and since determination of thiosulphate in a sample is quite cumbersome, the iodine-thiosulphate method (Method-2) was adopted and used for all the H<sub>2</sub>S analysis.

As for  ${\rm CO}_2$  Method-6 was found to be good. It reproduced data in the literature reasonably well and also gave reproducible results. Its only disadvantage is that it is slightly cumbersome. Because of absence of any other reliable and less cumbersome technique for  ${\rm CO}_2$  analysis in the literature, this method was used for all  ${\rm CO}_2$  determinations.

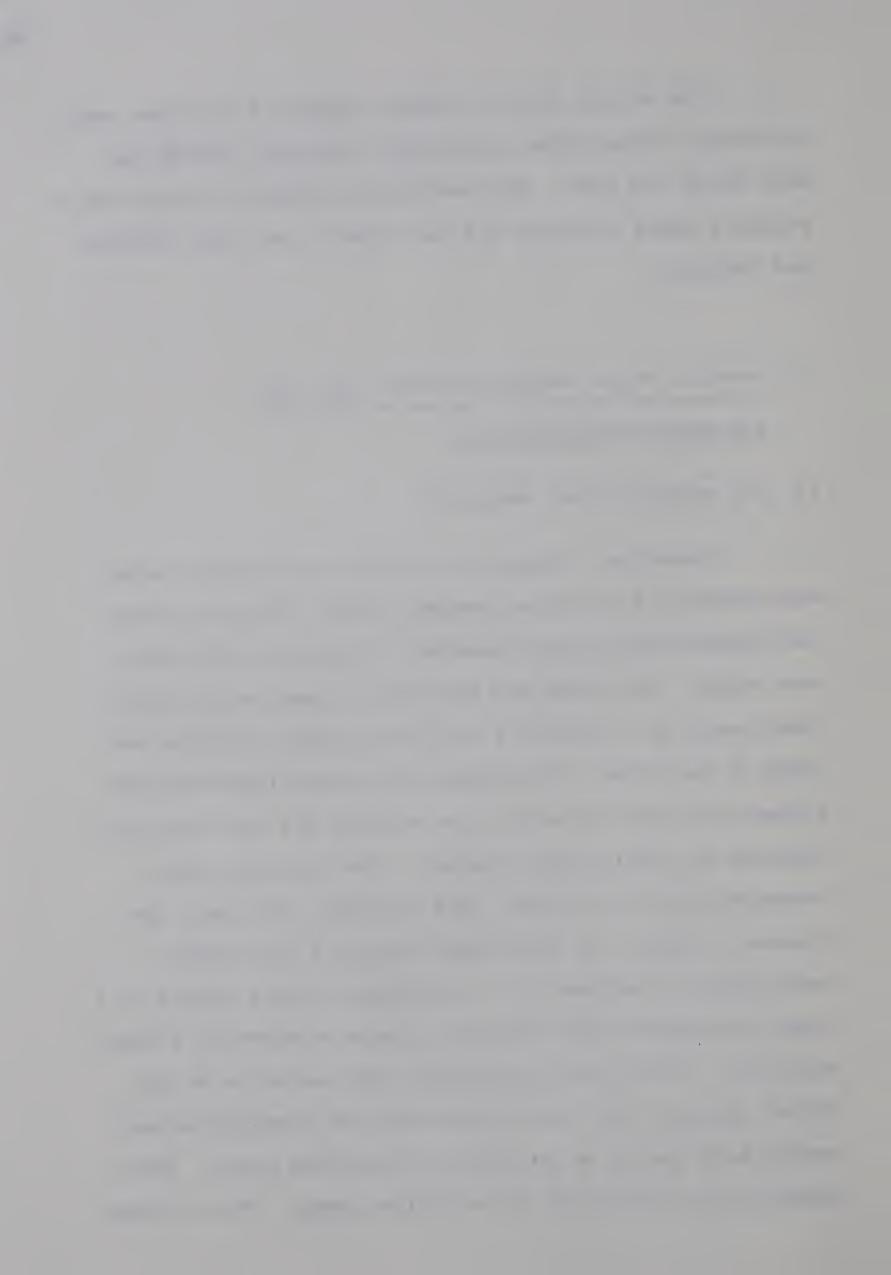


The method used for amine analysis is the one used by Girdler Corporation, Louisville, Kentucky (SM-1M for MEA; SM-1D for DEA). This method was tested by preparing a standard amine solution and was found to be very accurate and reliable.

- G. Details of the Methods Used for CO<sub>2</sub>, H<sub>2</sub>S

  And Amine Determinations:
- a) CO<sub>2</sub> Determination (Method-6)

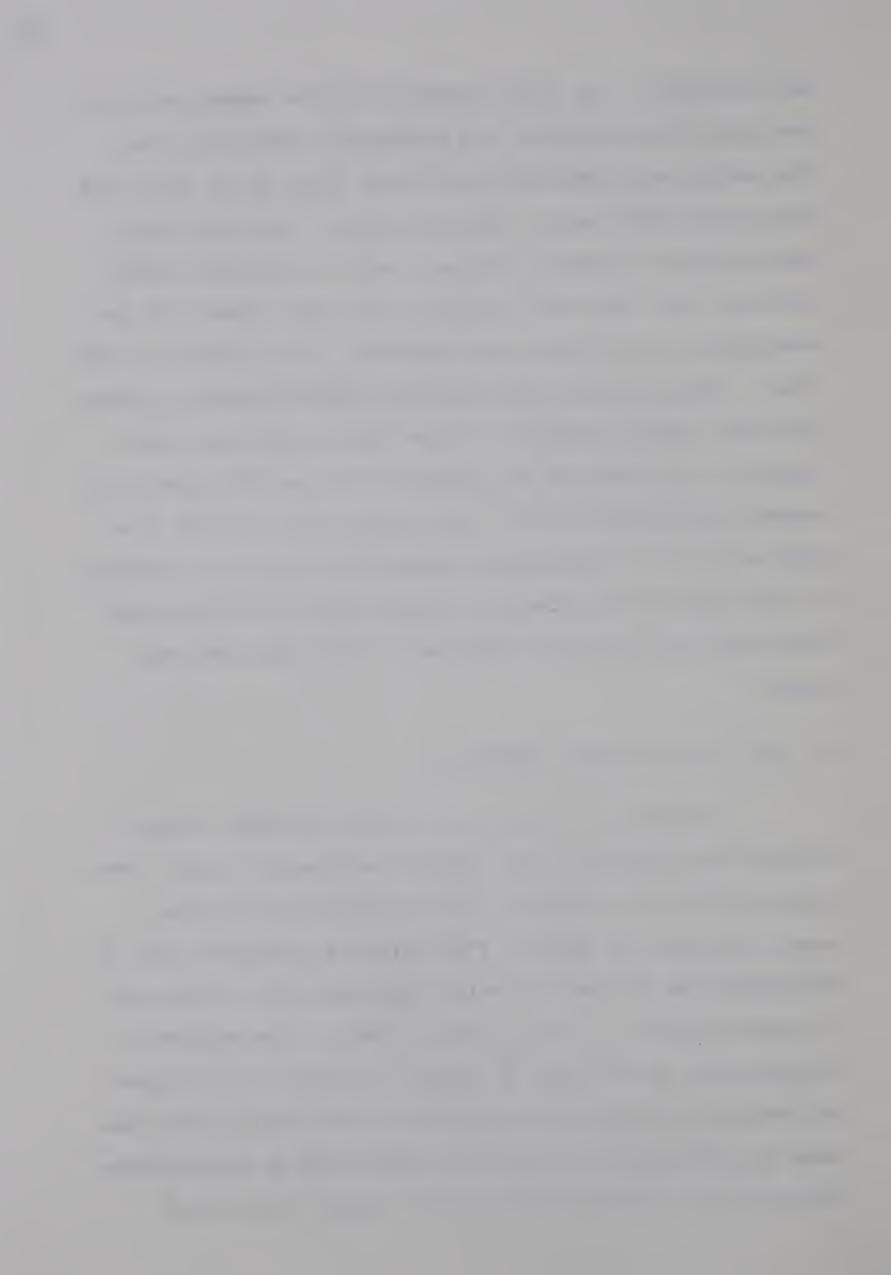
Procedure: About 20 to 25 ml of distilled water was heated in a 250 ml erlenmeyer flask. Once the water had started boiling approximately 2 grams of solid BaCl<sub>2</sub> The flask was swirled to dissolve the BaCl2. were added. Immediately by a syringe 2 ml of the sample solution was added to the flask. The flask was removed from heat and allowed to stand for about five minutes for the white precipitate to settle down somewhat. The flask was then stoppered and cooled under cold tap water for about ten Three 7 cm 41 Whatman ashless filter papers minutes. were placed in series in a 7 cm Büchner funnel placed in a large erlenmeyer flask with the sidearm attached to a water aspirator. Slowly the precipitate was poured on to the filter papers. The flask containing the precipitate was washed with two 25 ml portions of distilled water. Each washing was transferred to the filter paper. The filtrate



was discarded. The filter papers with the washed precipitate were transferred to the erlenmeyer flask which had the precipitate previously and about fifty ml of distilled water were added to it. The contents of the flask were swirled with a magnetic stirrer, until the filter paper had been torn into small pieces (this puts almost all the precipitate in solution and therefore, it is easier to titrate). Approximately five drops of modified methyl orange indicator (Methyl Orange - Xylene Cyanol solution) were added to the flask and the mixture titrated with about 0.1 normal hydrochloric acid. The mixture was titrated to a grey end point. Any barium carbonate precipitate sticking to the sides of the flask was washed down with distilled water and the titration continued to the same grey end point.

# b) H<sub>2</sub>S Determination (Method-2)

Procedure: 20 ml of 0.1 normal standard iodine solution was pipetted into a 500 ml erlenmeyer flask. The proper excess of sulphuric acid for the size of amine sample aliquot was added. (The ratio of sulphuric acid to DEA should be at least 18 moles  ${\rm H_2SO_4}$  per mole of DEA and 11 moles sulphuric acid per mole of MEA). The magnetic stirring bar was now put in and by a syringe 2 ml aliquot of sample was added while stirring. The excess iodine was back titrated with standard 0.1 normal sodium thiosulphate solution to a light yellow colour. About 5 ml of 0.2



percent starch indicator solution was now added and the titration continued to the change from blue-black to water-white colour.

#### c) MEA (or DEA) Determination:

Procedure: To an erlenmeyer flask containing about 100 ml of distilled water, two ml of sample solution were added. A few drops of methyl red indicator were added until the colour was distinctly yellow. The solution was then titrated using ca. 1 normal sulphuric acid. The end point was indicated by change in colour of solution from yellow to pink.



#### CHAPTER II

#### EXPERIMENTAL RESULTS AND THEIR COMPARISON

This chapter presents in graphical form, the expermental data obtained in this work.

made for conditions of solution strength and temperatures for which some data were available in the literature.

Measurements were made for pure H<sub>2</sub>S and pure CO<sub>2</sub> in 2.5 N

MEA at 80° and 100°C. For the two 100°C isotherms and the 80°C isotherm for H<sub>2</sub>S, some data points, for low loadings of acid gases (ca 0.1 moles/mole of MEA and less), have been obtained by Jones et al. 9, and Garst and Lawson 33.

These points have been plotted on the same figures. In this work, data were also obtained for mixtures of CO<sub>2</sub> and H<sub>2</sub>S in 5 N MEA at 100°C. The loadings of H<sub>2</sub>S and CO<sub>2</sub> were less than ca. 0.12 moles/mole of MEA. For these low acid gas concentrations, no data have been published to date.

Figures 2 and 3 present the 80°C isotherms for pure H<sub>2</sub>S and CO<sub>2</sub> in 2.5 N MEA. Figures 4 and 5 show the 100°C isotherms for pure H<sub>2</sub>S and CO<sub>2</sub> in 2.5 N MEA. Smoothed mixture data, for CO<sub>2</sub> and H<sub>2</sub>S in 5 N MEA at 100°C, are plotted in Figures 6 and 7. The raw experimental data are tabulated in Appendix B.



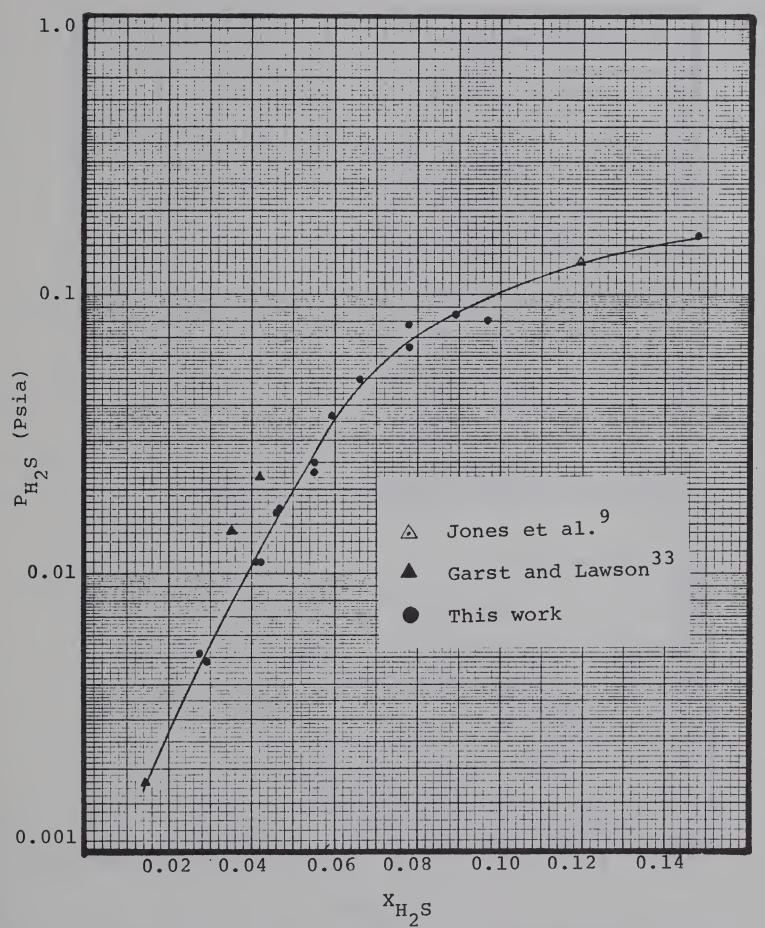


Figure 2 - Solubility of H<sub>2</sub>S in 2.5 N MEA Solution at 80°C.

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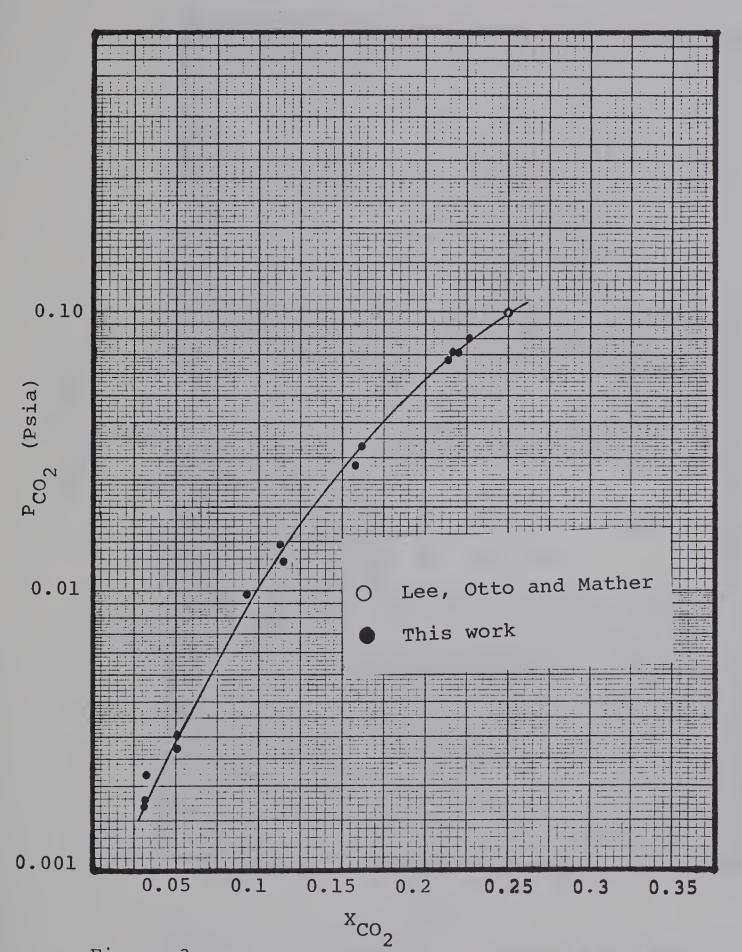


Figure 3 - Solubility of CO<sub>2</sub> in 2.5 N MEA Solution at 80°C.



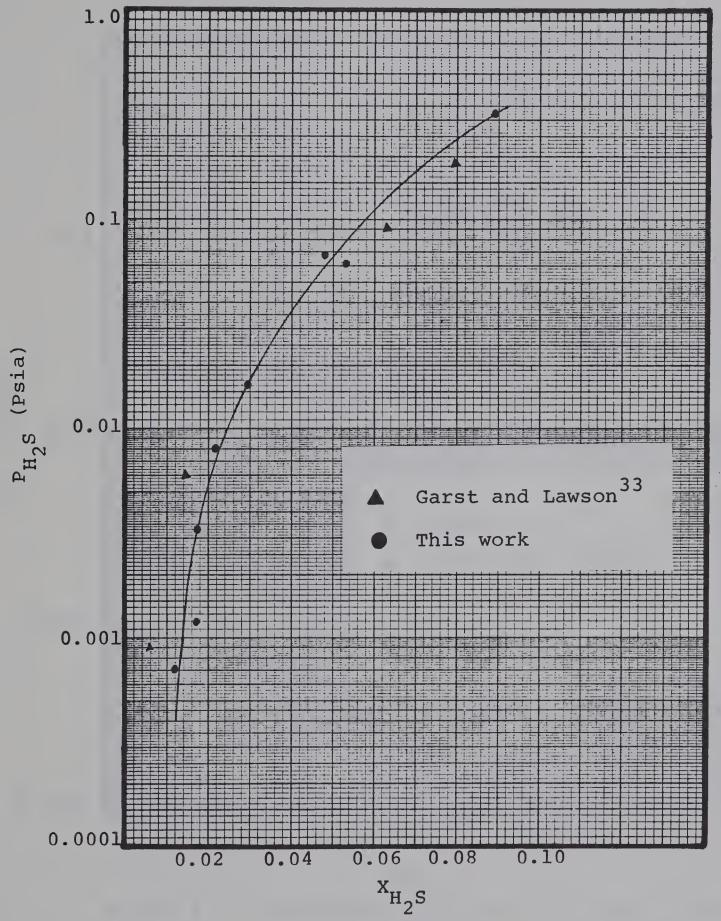


Figure 4 - Solubility of H<sub>2</sub>S in 2.5 N MEA Solution at 100°C.



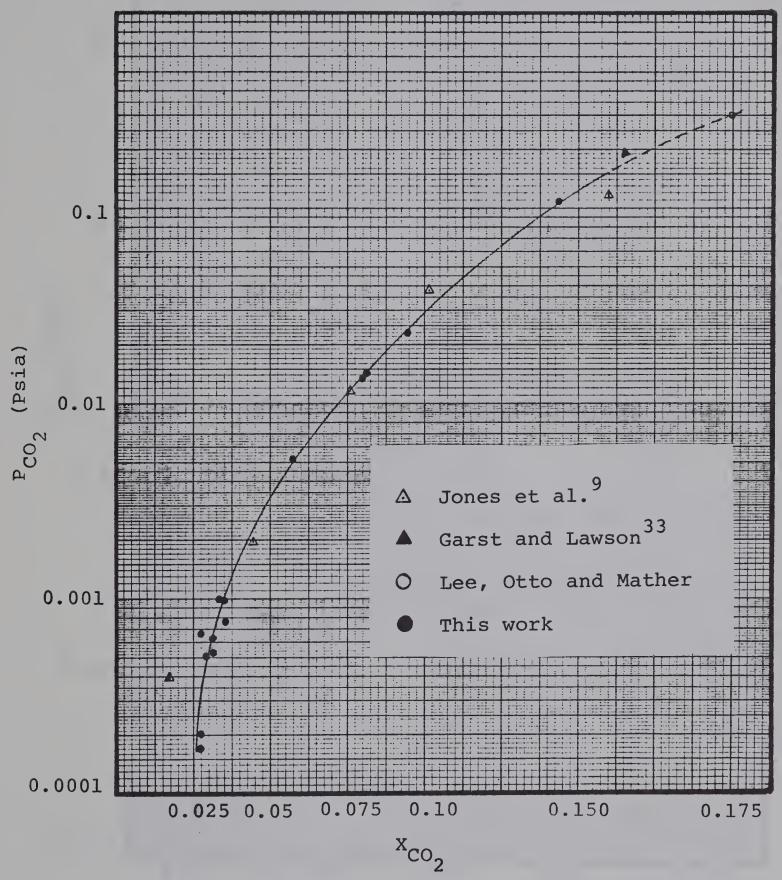


Figure 5 - Solubility of CO<sub>2</sub> in 2.5 N MEA Solution at 100°C.



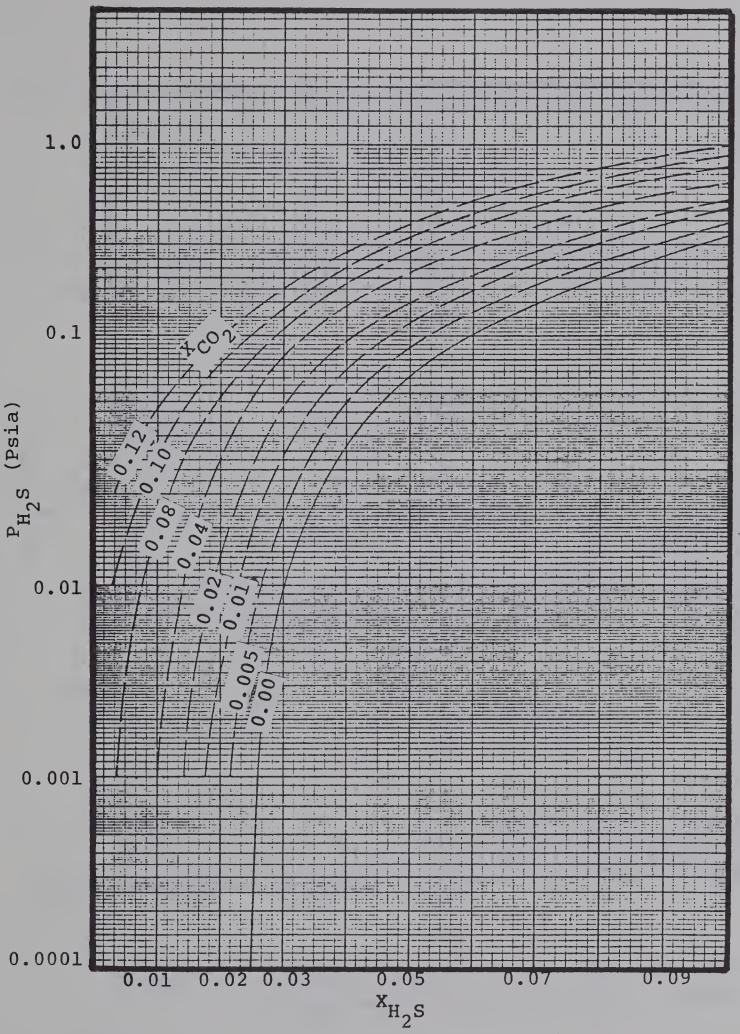


Figure 6 - Effect of CO<sub>2</sub> on the Partial Pressure of H<sub>2</sub>S Over 5 N MEA Solution at 100°C.



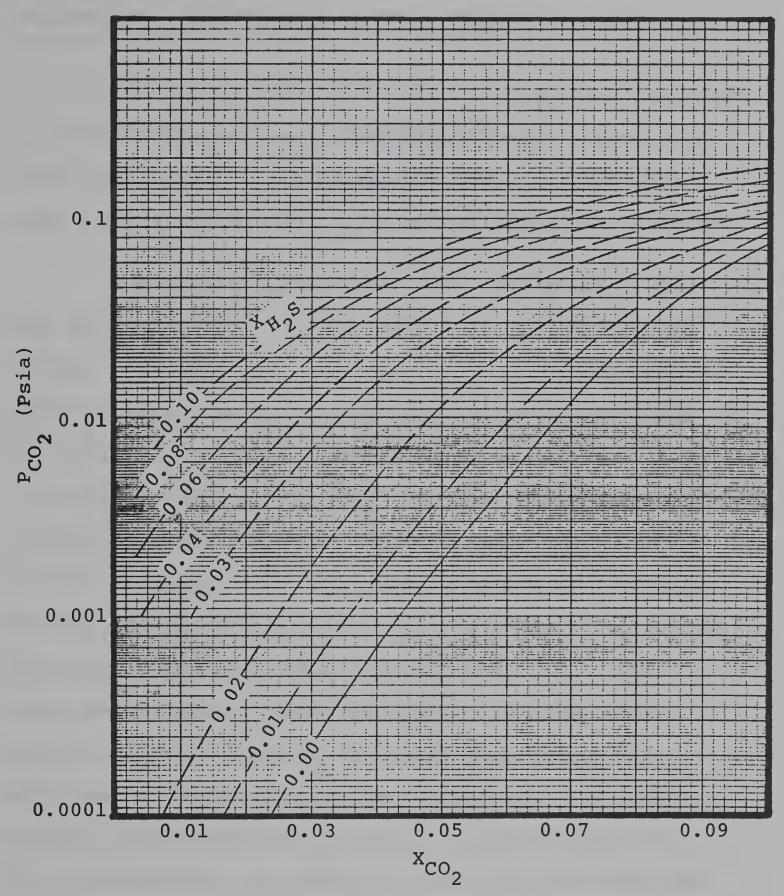


Figure 7 - Effect of H<sub>2</sub>S on the Partial Pressure of CO<sub>2</sub> Over 5 N MEA Solution at 100°C.



#### CHAPTER III

# THEORETICAL PREDICTION OF PARTIAL PRESSURES OF H2S and CO2

While the solubility data are useful in themselves, it is desirable to have a computer-oriented correlation which reproduces the experimental results. It would also be useful for regions where no data are presently available.

A number of researchers have attempted to correlate the solubility data for CO2 and/or H2S in ethanolamine solutions. A common starting point for all the thermodynamic models proposed so far is the postulation of reactions occuring in the solution. For simple systems, i.e. systems containing either H<sub>2</sub>S or CO<sub>2</sub> in aqueous ethanolamine (EA) solution, correlations have been proposed by different Atwood et al. 1 proposed a correlation for predicting partial pressures of H2S in aqueous ethanolamine solutions based on chemical reactions taking place in the solution. Klyamer 11 made slight modifications in the above correlation and has also made some comparisons with experimental data. Klyamer and Kolesnikova 12 discussed a general mathematical description of experimental data for the thermodynamic equilibrium in the CO2-water-MEA(DEA) In postulating the equilibrium equations they systems. have accepted the assumptions made by Atwood et al. 1. They found that the maximum error in the calculated values



compared to the experimental ones for a given set of conditions was not larger than 20 percent of CO<sub>2</sub> partial pressure. Theoretical treatment of equilibria for the absorption of CO<sub>2</sub> into aqueous ethanolamine solutions has also been discussed by Danckwerts and McNeil<sup>4</sup>.

More recently Klyamer et al. 13 have proposed a thermodynamic model for predicting equilibrium partial pressures of acid gases in aqueous ethanolamine solutions. They have obtained equations which describe the functional dependence between the partial pressure of the acid gas components and the composition of the solution at various temperatures. In essence, their model combines the chemical equations postulated for the simple systems, H<sub>2</sub>S-water-EA and CO<sub>2</sub>-water-EA, and also incorporates the assumptions made for these simple systems by other authors.

Most recently (while this work was in progress)

Kent and Eisenberg<sup>10</sup> presented a modified version of the Klyamer et al.<sup>13</sup> model. This model is essentially based on postulation of similar reactions as those of the Klyamer et al.<sup>13</sup> model; however, all the non-idealities have been incorporated into only two parameters.

Both the Klyamer et al. 13 and the Kent and Eisenberg 10 Models are discussed in detail in the following pages along with the modification in Klyamer et al. model.



## A. Correlation Based on the Thermodynamic Model of Klyamer et al. 13:

The assumptions made in postulating the chemical reactions are listed below:

- a) The salts (bisulphides, carbonates and carbamates) which are created by the absorption of  ${\rm H_2S}$  and  ${\rm CO_2}$  are fully dissociated  $^{1,11,12}$ .
- b) The activity coefficients of different ions in solution are equal and independent of temperature 1.
  - c) The activity of water is equal to its molarity 1.
- d) The physical solubility of  $CO_2$  or  $H_2S$  is not changed by the addition of ethanolamine (EA) and salts of  $EA^{1,12}$ .

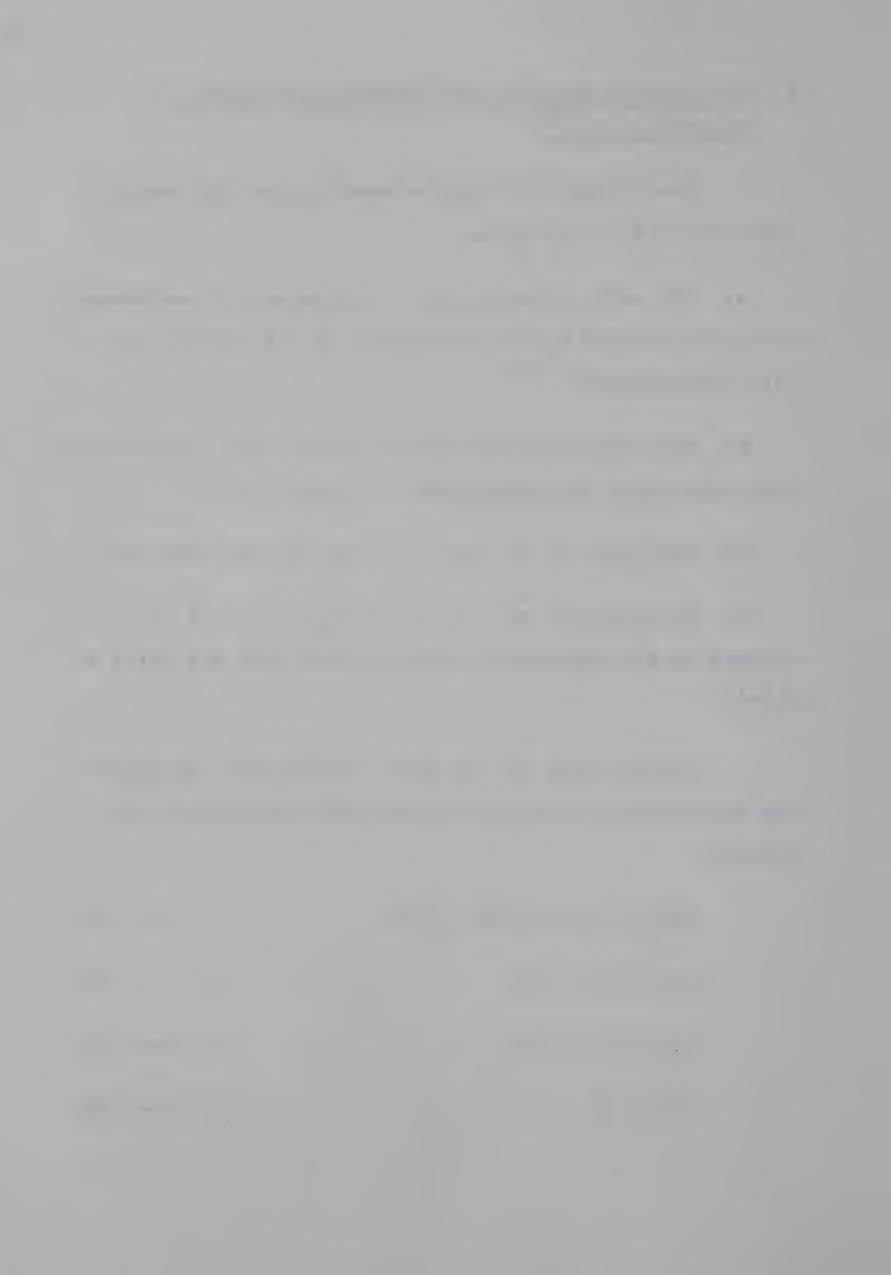
On the basis of the above assumptions the following reactions for the  ${\rm H_2S-CO_2}{\text{-water-MEA}}$  systems can be written:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$
 -----(a)

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$
 -----(c)

$$HS^- \rightleftharpoons H^+ + S^{2-}$$
 -----(d)



$$2RNH_2 + CO_2 \rightleftharpoons RNH_3^+ + RNHCOO \longrightarrow -----(e)$$

$$CO_2 + H_2O \implies H^+ + HCO_3^-$$
 -----(f)

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
 -----(g)

where R stands for  $-CH_2-CH_2-OH$  group. Analogous equations may be written (to represent the reactions) for the  $H_2S-CO_2$ -water-DEA system.

The following balance equations for the reacting compounds can be formed:

Charge balance (or Electroneutrality) equation:

$$[RNH_3^+] + [H^+] = [HCO_3^-] + [RNHCOO] + 2[CO_3^{2-}] + [OH^-] + [HS^-] + 2[S^{2-}]$$

Mass balance equations:

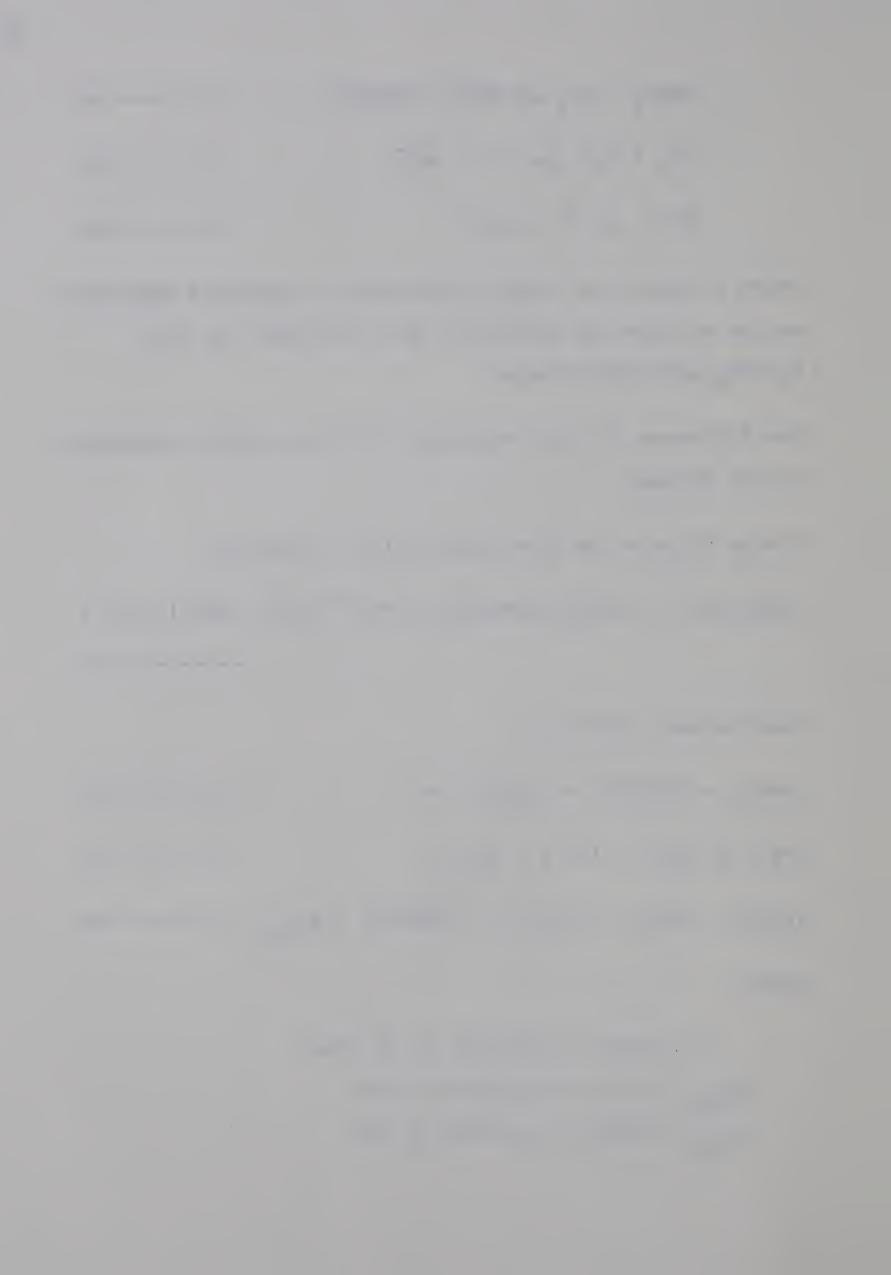
$$[RNH_2] + [RNHCOO] + [RNH_3^+] = m$$
 -----(2)

$$[HS^{-}] + [H_{2}S] + [S^{2-}] = mX_{H_{2}S}$$
 -----(3)

$$[HCO_3^-] + [CO_2] + [CO_3^{2-}] + [RNHCO_0^-] = mX_{CO_2}^-$$
 -----(4)

where,

$$m = moles of EA/1000 gm of water$$
 $X_{CO_2} = moles of CO_2/mole of EA$ 
 $X_{H_2S} = moles of H_2S/mole of EA$ 



 $[C_i]$  = moles of compound (or ion)  $C_i/1000$  gm of water (Molality).

The following thermodynamic equilibrium constant expressions can also be written:

$$K_i = \frac{\gamma^2}{\alpha \alpha^2} \frac{[RNH_3^+] [OH^-]}{[RNH_2]}$$
 -----(5)

$$K_{W} = \frac{\gamma^{2} [H^{+}] [OH^{-}]}{\alpha}$$
 -----(6)

$$K_{1C} = \frac{\gamma^2 [H^+] [HS^-]}{[H_2S]}$$
 -----(7)

$$K_{2C} = \frac{\gamma [H^+] [S^{2-}]}{[HS^-]}$$
 -----(8)

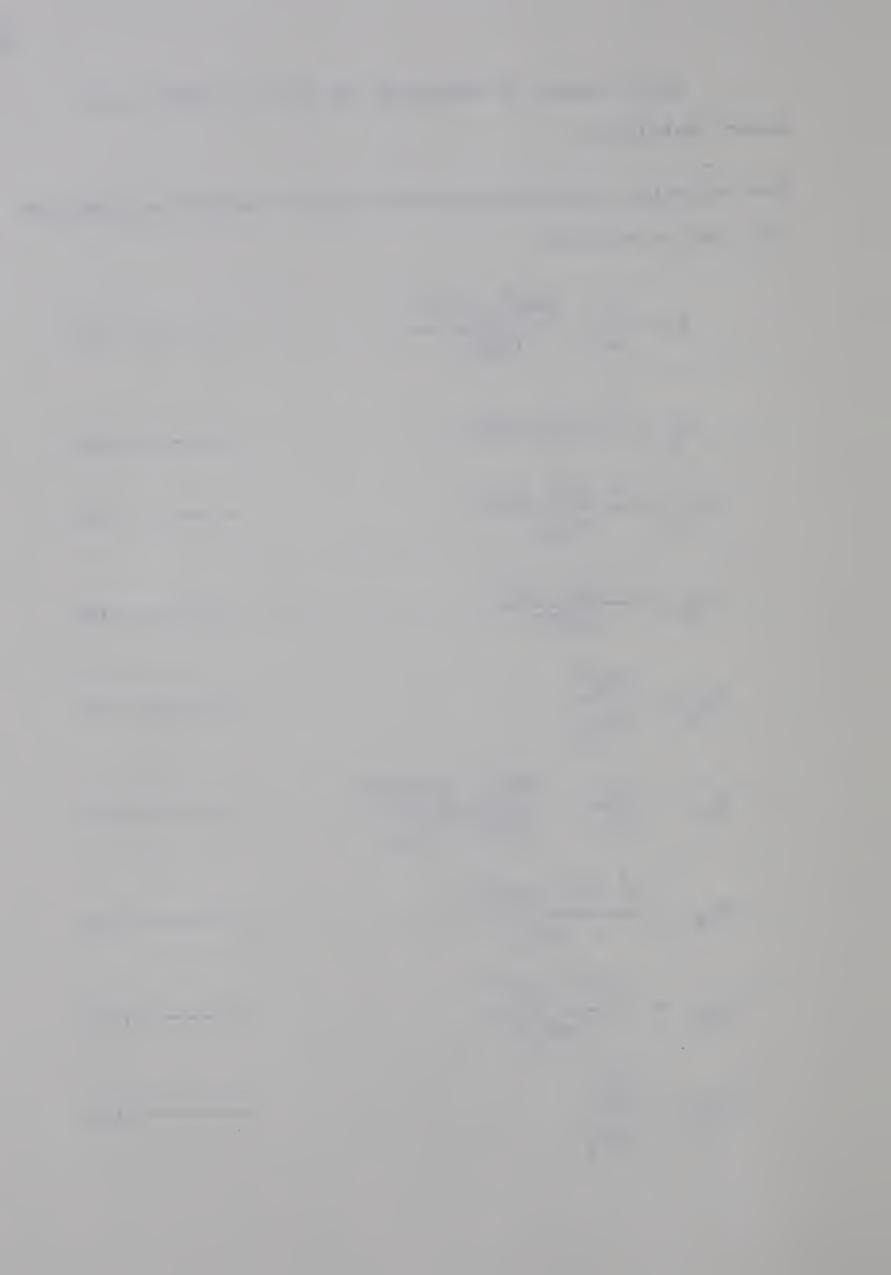
$$H_{H_2S} = \frac{[H_2S]}{P_{H_2S}}$$
 -----(9)

$$K_{\rm m} = \frac{\gamma^2}{a^2 \alpha^2} \cdot \frac{[{\rm RNH}_3^+] [{\rm RNHCool}]}{[{\rm RNH}_2]^2 P_{\rm CO}_2}$$
 -----(10)

$$K_{1Y} = \frac{\gamma^2 [H^+] [HCO_3^-]}{\alpha [CO_2]}$$
 -----(11)

$$\kappa_{2Y} = \frac{\gamma \ [H^{+}] \ [CO_{3}^{2-}]}{[HCO_{3}^{-}]}$$
 -----(12)

$$H_{CO_2} = \frac{[CO_2]}{P_{CO_2}} -----(13)$$



WHERE

[RNHCOO], [HCO $_3$ ], [CO $_3$ <sup>2-</sup>], [CO $_2$ ], [H $_2$ S], [RNH $_3$ <sup>+</sup>], [RNH<sub>2</sub>], [OH $^{-}$ ], [HS $^{-}$ ] and [S $^{2-}$ ] are respectively, the concentrations (molalities) of the carbamate, bicarbonate, carbonate ions, the physically dissolved CO2 and H2S, concentrations of ionized and un-ionized ethanolamine, hydroxyl ions, hydrogen ions, bisulphide and sulphide ions. PCO2 and  $P_{H_2S}$  are the partial pressures of  $CO_2$  and  $H_2S$  respectively in mm of mercury; Km, K1Y, K2Y, Ki, Kw, HCO2, HH2S,  ${
m K}_{1{
m C}}$  and  ${
m K}_{2{
m C}}$  are the equilibrium constants for the formation of the carbamate, the first and second dissociation constants for H2CO3 (carbonic acid), EA ionization constant, water dissociation constant, the inverted Henry's constants for CO, and H,S solubility in water, the first and second constants for H<sub>2</sub>S dissociation. The average coefficient for the ion activity is given the symbol  $\gamma$ ,  $\alpha$  is the coefficient for the water activity and a is the ratio between the un-ionized ethanolamine activity and the activity of water.

Atwood et al. have shown that for the system H<sub>2</sub>S-water-EA the form of the dependence of the average value of the activity coefficients on their concentration can be taken as the same for all ions. Klyamer et al. 13 have accepted this dependence of the average value of



activity coefficient of all ions on the ionic concentration for the system  $H_2S-CO_2$ -water-EA by the formulation of equations (5) to (8) and (10) to (12). Atwood et al. obtained the average value of activity coefficient,  $\gamma$ , by assuming that the amine salts are similar to ammonium salts. They have correlated  $\gamma$  as a function of ionic strength of the solution. The ionic strength,  $\mu$ , is defined as:

$$\mu = \sum_{i} m_{i} z_{i}^{2}$$

 $m_i = molality of each ion.$ 

Z; = electrical charge on each ion.

The values for the dependence of the correction factor,  $\alpha$ , on the concentration of the free ethanolamine and the values of  $K_{\rm W}$ ,  $K_{\rm 1C}$ ,  $K_{\rm 2C}$ ,  $K_{\rm 2Y}$ ,  $H_{\rm CO_2}$  and  $H_{\rm H_2S}$  in the range of tempereratures 25 to 120°C were taken from the work of Atwood et al. Values of  $K_{\rm i}$ ,  $K_{\rm m}$  and  $K_{\rm 1Y}$  as functions of temperature have been taken from earlier publications  $^{11,12}$ .

The analysis of equations (1) to (13) leads to the conclusion that the most important parameters which enter into many reactions are the so called degrees of sulphidation  $(X_{H_2S})$  and carbonation  $(X_{CO_2})$ . It has been shown that the concentration of the ions  $S^{2-}$  and  $H^+$  can be neglected for all practical cases in equations (1) to (3)  $^{11,12}$ . It is necessary to take  $[CO_3^{\ 2-}]$  and  $[OH^-]$  into account only at very low  $X_{CO_2}$  or  $X_{H_2S}$  (i.e. for  $X_{CO_2}$  or  $X_{H_2S}$ 



approximately equal to 0.01 mole/mole of EA). If these simplifications are taken into account, the simultaneous solution of equations (1) to (13) allows derivation of expressions for the calculation of the equilibrium partial pressures of  $\rm CO_2$  and  $\rm H_2S$  if the liquid phase composition and temperature are known. These expressions (as derived in Appendix C) are:

$$P_{H_2S} = \frac{K_W}{K_i K_{1C} H_{H_2S}} \cdot \frac{\gamma^2}{\alpha \alpha} \cdot \frac{A(A+B)}{(m-z-A-B)}$$
 -----(14)

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{\alpha^2 \alpha^2} \cdot \frac{z (A+B)}{(m-z-A-B)^2}$$
 -----(15)

and

A = m-z-B- 
$$\frac{K_{i} K_{1Y} H_{CO_{2}}}{K_{m} K_{w}} \cdot \frac{z}{\alpha (B-z)}$$
 -----(16)

where

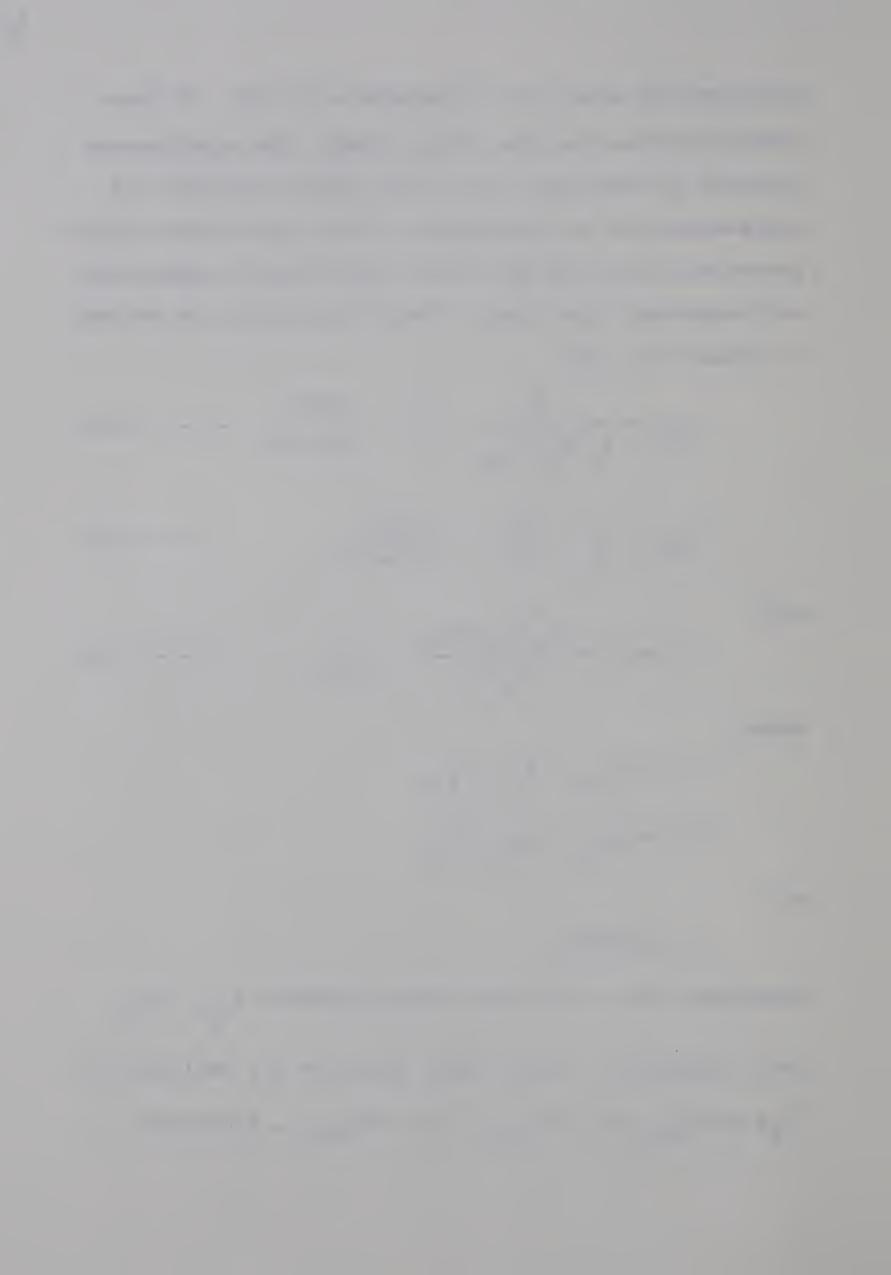
$$A = m X_{H_2S} - H_{H_2S} P_{H_2S}$$

$$B = m X_{CO_2} - H_{CO_2} P_{CO_2}$$

and

$$z = [RNHCOO]$$

Equations (14) to (16) have three unknowns;  $P_{H_2S}$ ,  $P_{CO_2}$  and z ([RNHCO $\bar{O}$ ]). Since these equations are implicit in  $P_{H_2S}$  and  $P_{CO_2}$  [A = f( $P_{H_2S}$ ); B = f( $P_{CO_2}$ )], iterative



techniques have to be used for their solution.

For a degree of saturation of solutions smaller than 0.7 moles/mole of EA, the physical solubility of  $\rm H_2S$  and  $\rm CO_2$  can be neglected in the balance equations  $^{1,11,12}$ . It can also be assumed that for  $\rm X_{\rm H_2S}$  plus  $\rm X_{\rm CO_2}$  between 0.05 and 0.7 moles/mole of EA,  $\rm CO_2$  will exist as RNHCOO and  $\rm HCO_3^-$  ions and  $\rm H_2S$  as  $\rm HS^-$  ions. If these simplications are taken into account, equations (14) to (16) can be simplified to:

$${}^{P}_{H_{2}S} = \frac{K_{W}}{K_{1}C} \cdot \frac{\gamma^{2}}{M_{2}S} \cdot \frac{mX_{H_{2}S} (X_{H_{2}S} + X_{CO_{2}})}{\left\{ \frac{[HCO_{3}]}{m} + 1 - X_{H_{2}S} - 2X_{CO_{2}} \right\}^{2}}$$

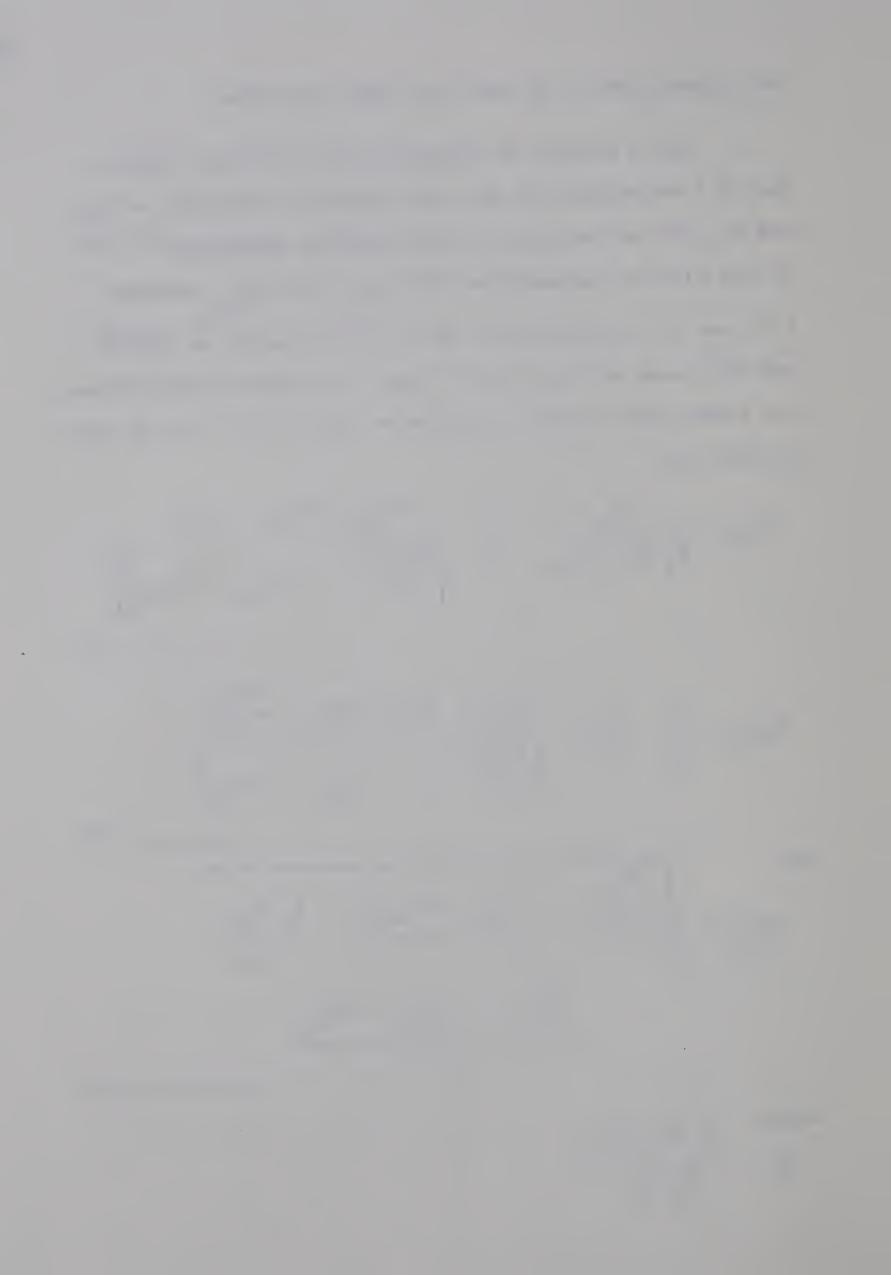
$$P_{CO_{2}} = \frac{1}{K_{m}} \cdot \frac{\gamma^{2}}{\alpha^{2} \alpha^{2}} \cdot \frac{(X_{H_{2}S} + X_{CO_{2}})(X_{CO_{2}} - \frac{[HCO_{3}]}{m})}{\left\{\frac{[HCO_{3}]}{m} + 1 - X_{H_{2}S} - 2X_{CO_{2}}\right\}^{2}}$$
(18)

and 
$$[HCO_{3}^{-}] = \sqrt{ \left( \frac{\frac{K_{I}}{a^{m}} + 1 - X_{H_{2}S} - 2X_{CO_{2}}}{2} \right)^{2} + \frac{K_{I} X_{CO_{2}}}{a^{m}} }$$

$$- \frac{\frac{K_{I}}{a^{m}} + 1 - X_{H_{2}S} - 2X_{CO_{2}}}{2}$$

$$- - - - - - - - - - - - - (19)$$

where
$$K_{I} = \frac{K_{i} K_{1Y} H_{CO_{2}}}{K_{w} K_{m}}$$



Equations (17) and (18) can be further simplified when  $X_{H_2S}$  plus  $X_{CO_2}$  are between 0.05 to 0.25 moles/mole of EA (concentrations characteristic of the regeneration process). For such cases the bicarbonate ion concentration can be neglected, and it can be assumed that  $CO_2$  exists only as carbamate ion. Therefore, if in equations (17) and (18),  $[HCO_3^-] = 0$ , the following expressions are obtained:

$$P_{H_2S} = \frac{K_W}{K_i K_{1C} H_{H_2S}} \cdot \frac{\gamma^2}{\alpha^{\alpha}} \cdot \frac{mX_{H_2S} (X_{H_2S} + X_{CO_2})}{(1 - X_{H_2S} - 2X_{CO_2})} ----- (20)$$

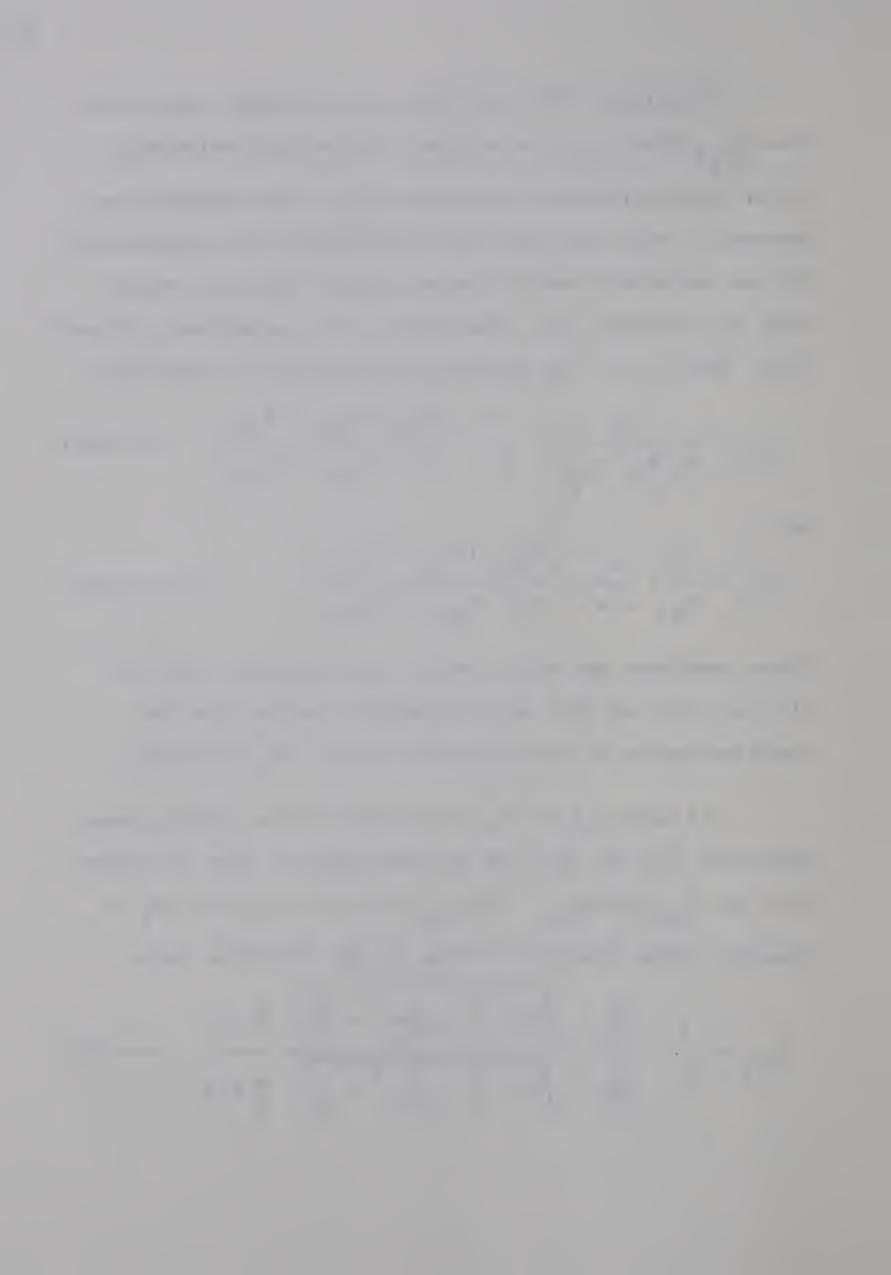
and

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{\alpha^2 \alpha^2} \cdot \frac{X_{CO_2} (X_{H_2S} + X_{CO_2})}{(1 - X_{H_2S} - 2X_{CO_2})^2} ------(21)$$

These equations are much simpler than equations (14) to (16) or (17) and (18) and, therefore, can be used for rapid estimates of partial pressures of the acid gases.

If only  $H_2S$  or  $CO_2$  is present in the liquid phase, equations (14) to (16) can be rearranged to give an expression for  $P_{H_2S}$  or  $P_{CO_2}$ . If  $X_{H_2S} = 0$ , i.e. if only  $CO_2$  is present, these equations reduce to the following form:

$$P_{CO_2} = \frac{B}{K_1} \cdot \frac{\frac{1}{2K_2} - \sqrt{(B - \frac{m}{2} - \frac{1}{2K_2})^2 + \frac{B}{K_2} + \frac{m}{2} - B}}{\frac{1}{2K_2} - \sqrt{(B - \frac{m}{2} - \frac{1}{2K_2})^2 + \frac{B}{K_2} - \frac{m}{2} + B}} ---- (22)$$



where

$$K_1 = \frac{K_i K_{1Y} H_{CO_2}}{K_w} \cdot \frac{\alpha \alpha^2}{\gamma^2}$$

and

$$K_2 = \frac{K_m K_w}{K_i K_{1Y} H_{CO_2}} \cdot \alpha$$

When  $X_{CO_2} = 0$ , i.e. if only  $H_2S$  is present, the following expression for calculation of  $P_{H_2S}$  is obtained 11.

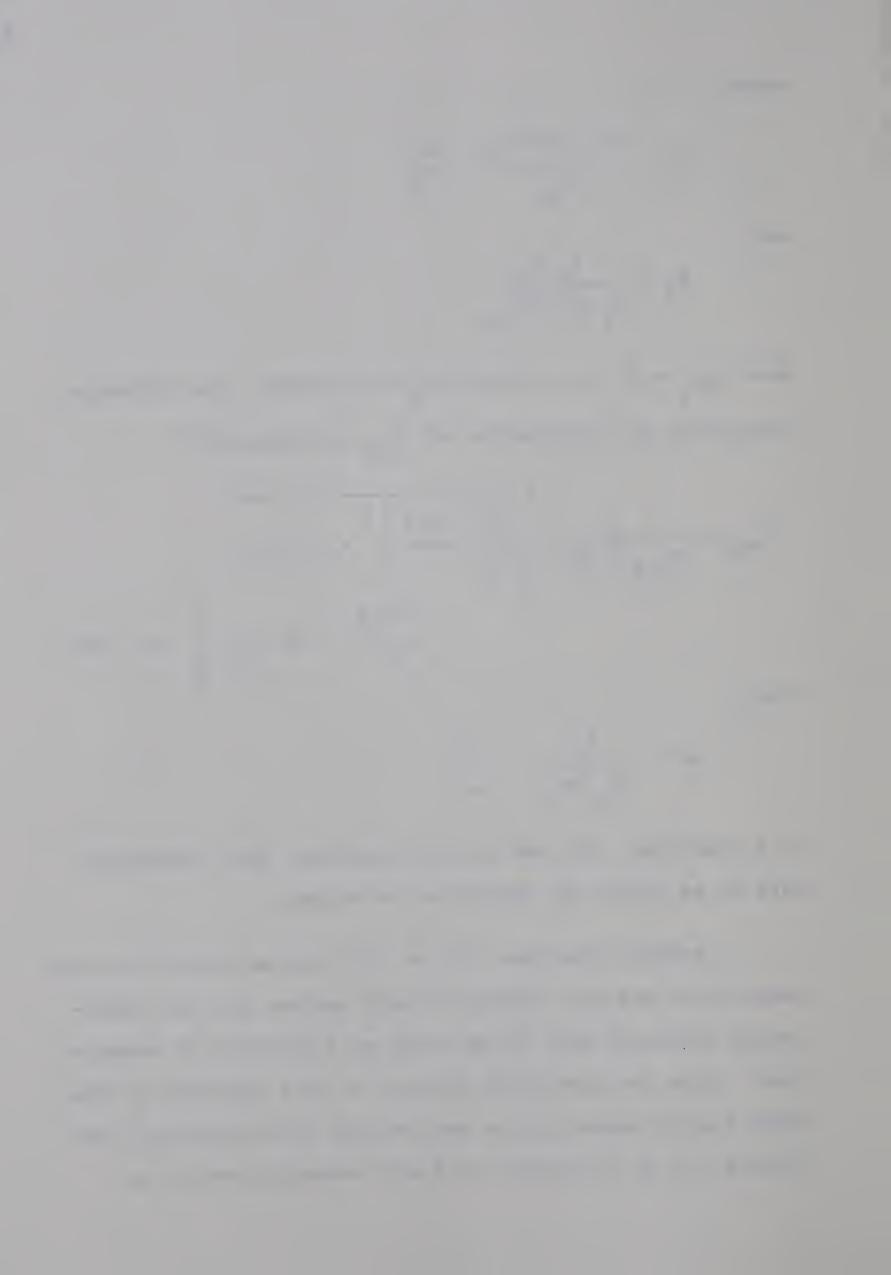
$$P_{H_{2}S} = \frac{m}{H_{H_{2}S}(1-K'')} \left[ \sqrt{\left(\frac{1-X_{H_{2}S}}{2}\right)^{2} + K'' X_{H_{2}S}} - K'' X_{H_{2}S} \right] ---- (23)$$

where

$$K'' = \frac{K_{W}}{K_{1C} K_{i}} \cdot \frac{\gamma^{2}}{\alpha \alpha}$$

Both equations (22) and (23) are implicit and, therefore, have to be solved by iterative techniques.

Before equations (14) to (23) can be solved for any temperature and any loading of acid gas(es) all the equilibrium constants have to be known as a function of temperature. Also the correction factor,  $\alpha$ , as a function of free ethanolamine concentration and average ionic activity coefficient ( $\gamma$ ) as a function of ionic strength have to be



known. In the literature  $^{1,11,12,13}$  the equilibrium constants as functions of temperature; the correction factor,  $\alpha$ , as a function of free EA concentration; and  $\gamma$  as a function of ionic strength have been presented in graphical form. These graphs were approximated by polynomials using the method of  $least\ squares$ , to be able to solve equations (14) to (16) by using a digital computer. The parameters for the polynomials are given in Appendix H.

The Modified Newton Raphson Method was used to solve the above equations. For each iteration a better estimate to  $P_{H_2S}$ ,  $P_{CO_2}$  and z was obtained by the following expressions:

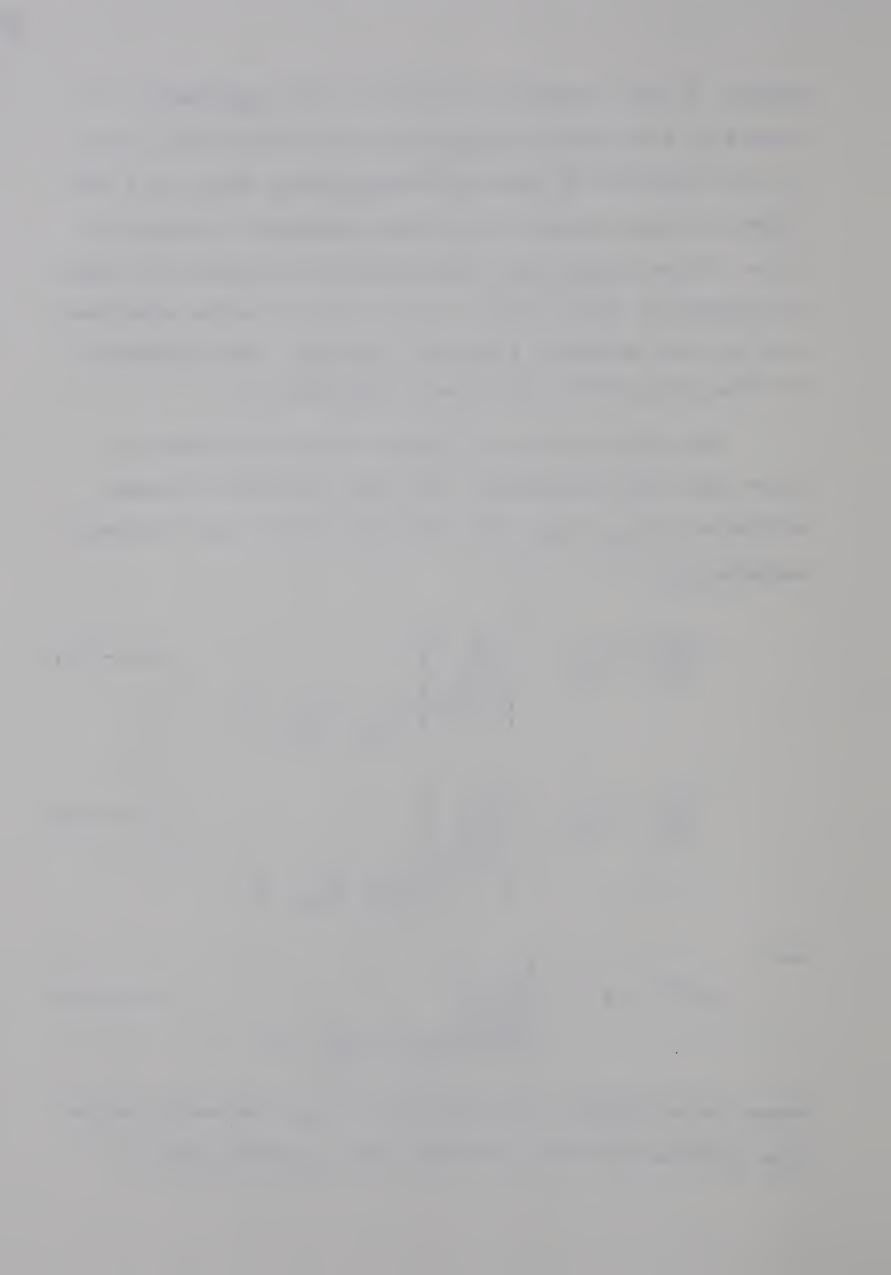
$$P_{H_2S}^{i+1} = P_{H_2S}^{i} - \begin{bmatrix} \frac{f_1}{\partial f_1} \\ \frac{\partial f_1}{\partial P_{H_2S}} \end{bmatrix} P_{H_2S}^{i}, P_{CO_2}^{i}, z^{i}$$
 -----(a)

$$P_{CO_2}^{i+1} = P_{CO_2}^{i} - \begin{bmatrix} \frac{f_2}{2} \\ \frac{\partial f_2}{\partial P_{CO_2}} \end{bmatrix}_{P_{H_2}^{i+1}, P_{CO_2}^{i}, z^{i}}$$
 -----(b)

and

$$z^{i+1} = z^{i} - \begin{bmatrix} \frac{f_3}{\partial f_3} \\ \frac{\partial f_3}{\partial z} \end{bmatrix} P_{H_2S}^{i+1}, P_{CO_2}^{i+1}, z^{i}$$
 -----(c)

where the variables superscripted i+l are the better estimates obtained from the previous ones, superscripted i.



Equations (14) to (16) are rearranged to give:

$$f_{1} = P_{H_{2}S} - \frac{K_{W}}{K_{1}K_{1}C} + \frac{\gamma^{2}}{\alpha^{2}} \cdot \frac{A(A+B)}{(m-z-A-B)}$$

$$f_{2} = P_{CO_{2}} - \frac{1}{K_{m}} \cdot \frac{\gamma^{2}}{\alpha^{2}\alpha^{2}} \cdot \frac{z(A+B)}{(m-z-A-B)^{2}}$$

$$f_{3} = z - \frac{\alpha K_{W} K_{m}}{K_{1}K_{1}Y} \cdot (B-z) \cdot (m-z-A-B)$$

The partial differentials of  $f_1$ ,  $f_2$  and  $f_3$  with respect to  $P_{\rm H_2S}$ ,  $P_{\rm CO_2}$  and z, respectively, are:

$$\frac{\partial f_{1}}{\partial P_{H_{2}S}} = 1 + \frac{K_{W}}{K_{i} K_{1C} H_{H_{2}S}} \left[ \frac{(m-z-A-B)(zA+B) + (A+B) H_{H_{2}S}}{(m-z-A-B)^{2}} \right]$$

$$\frac{\partial f_{2}}{\partial P_{CO_{2}}} = 1 + \frac{\gamma^{2}}{K_{m} \alpha^{2} \alpha^{2}} \cdot \frac{z_{CO_{2}} \left[ (m-z-A-B)^{2} + 2 (m-z-A-B) (A+B) \right]}{(m-z-A-B)^{4}}$$

$$\frac{\partial f_3}{\partial z} = 1 + \frac{\alpha K_w K_m}{K_i K_{1Y} H_{CO_2}} \cdot (m - 2z - A)$$

Equations (17) to (21) were used to obtain the initial estimates of  $P_{H_2S}$  and  $P_{CO_2}$ . These initial values along with an assumed value of z were used in equations (a) to (c) to obtain better estimates. Iteration with equations (a) to (c) was continued until the difference between two successive values of each of the three variables was less than 1 percent.



## B. Modifications in Klyamer et al. Model:

a) Partial pressures were substituted by fugacities in equations (9) and (13). This was considered necessary especially for low temperatures and high total pressures (pressures greater than 100 psia). The fugacity coefficient is defined as:

$$\phi_k = \frac{f_K}{P_K} \longrightarrow P_k = \frac{f_k}{\phi_k}$$

where

 $P_k$  = partial pressure of component k

 $f_k$  = fugacity of component k

 $\phi_k$  = fugacity coefficient for component k.

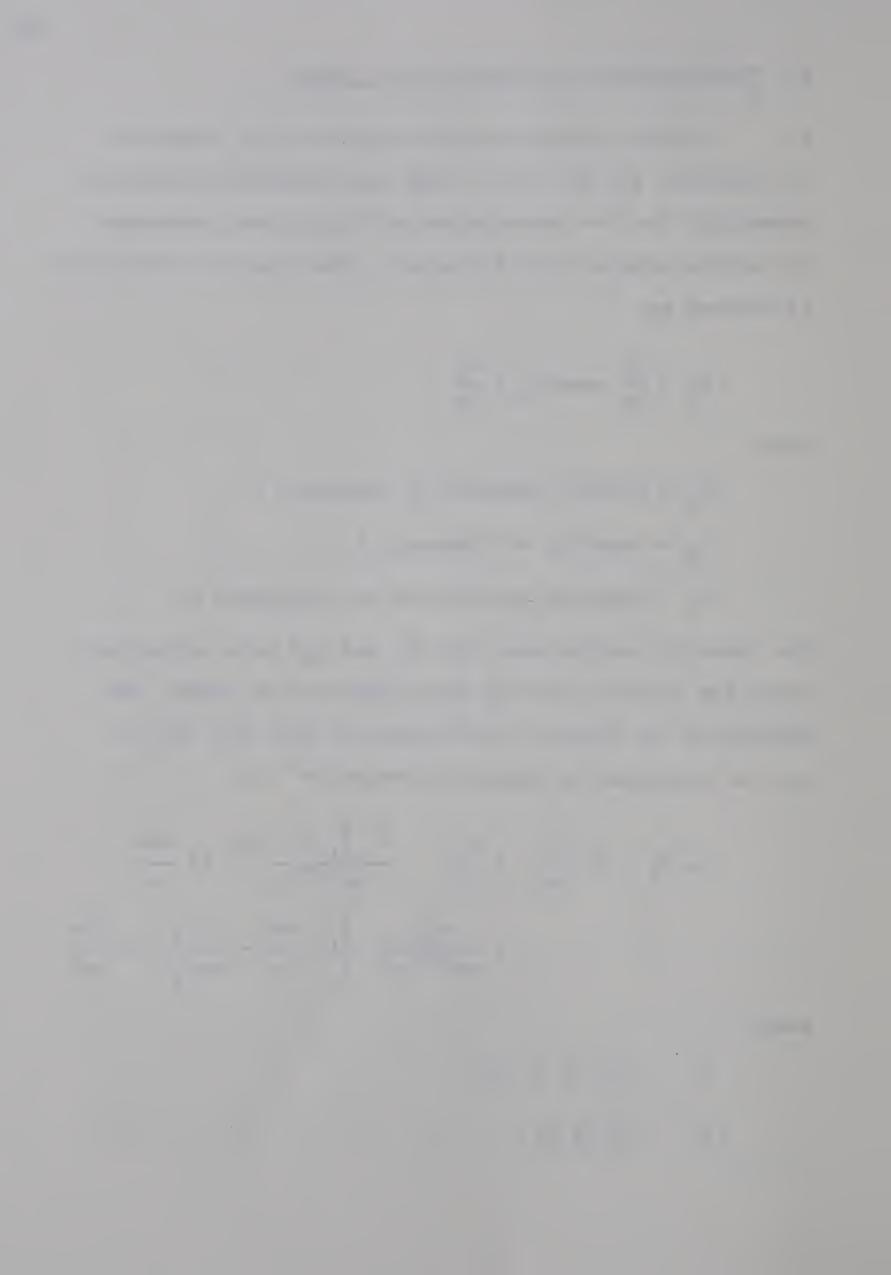
The fugacity coefficients for  ${\rm CO_2}$  and  ${\rm H_2S}$  were calculated using the *Modified Redlich-Kwong* equation of state. The expression for fugacity coefficient of each gas  $({\rm CO_2}$  or  ${\rm H_2S})$  as presented by Chueh and Prausnitz<sup>3</sup> is:

$$\ln \phi_{k} = \ln \frac{v}{v-b} + \frac{b_{k}}{v-b} - \frac{2 \sum_{i=1}^{m} y_{i} a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_{k}}{RT^{3/2} b^{2}} \left[ \ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT}$$

where

$$a = \sum_{ij} y_i y_j a_{ij}$$

$$b = \sum_{i} y_{i} b_{i}$$



$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj}) R^2 T_{C_{ij}}^{2.5}}{2 P_{C_{ij}}}$$

$$b_{i} = \frac{\Omega_{b_{i}}^{RT_{C_{i}}}}{P_{c_{i}}}$$

$$P_{C_{ij}} = \frac{z_{C_{ij}}^{R} T_{C_{ij}}^{T_{C_{ij}}}}{V_{C_{ij}}}$$

$$V_{c_{ij}} = \frac{1}{2} (V_{c_{i}}^{1/3} + V_{c_{j}}^{1/3})$$

$$z_{C_{ij}} = 0.291 - 0.08 \left(\frac{\omega_{i} + \omega_{j}}{2}\right)$$

$$T_{C_{ij}} = (T_{C_i} T_{C_j})^{\frac{1}{2}} (1 - k_{ij})$$

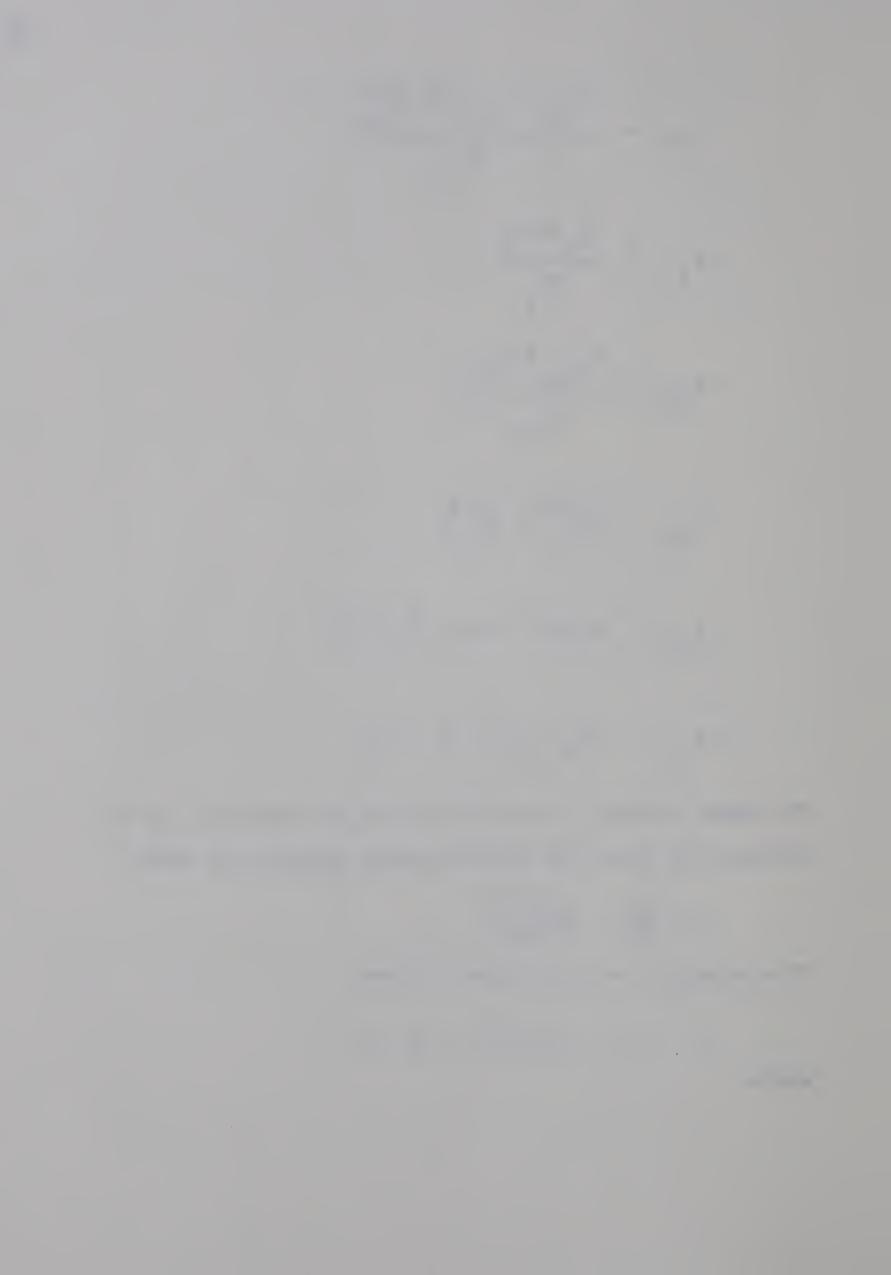
The molar volume, v, is that of the gas mixture, and is obtained by using the Redlich-Kwong equation of state,

$$P = \frac{RT}{v-b} - \frac{(a/T^{0.5})}{v(v+b)}$$

This equation is rearranged to give:

$$z^3 - z^2 + z(A-B-B^2) - AB = 0$$

where



$$A = \frac{aP}{R^2T^2}$$

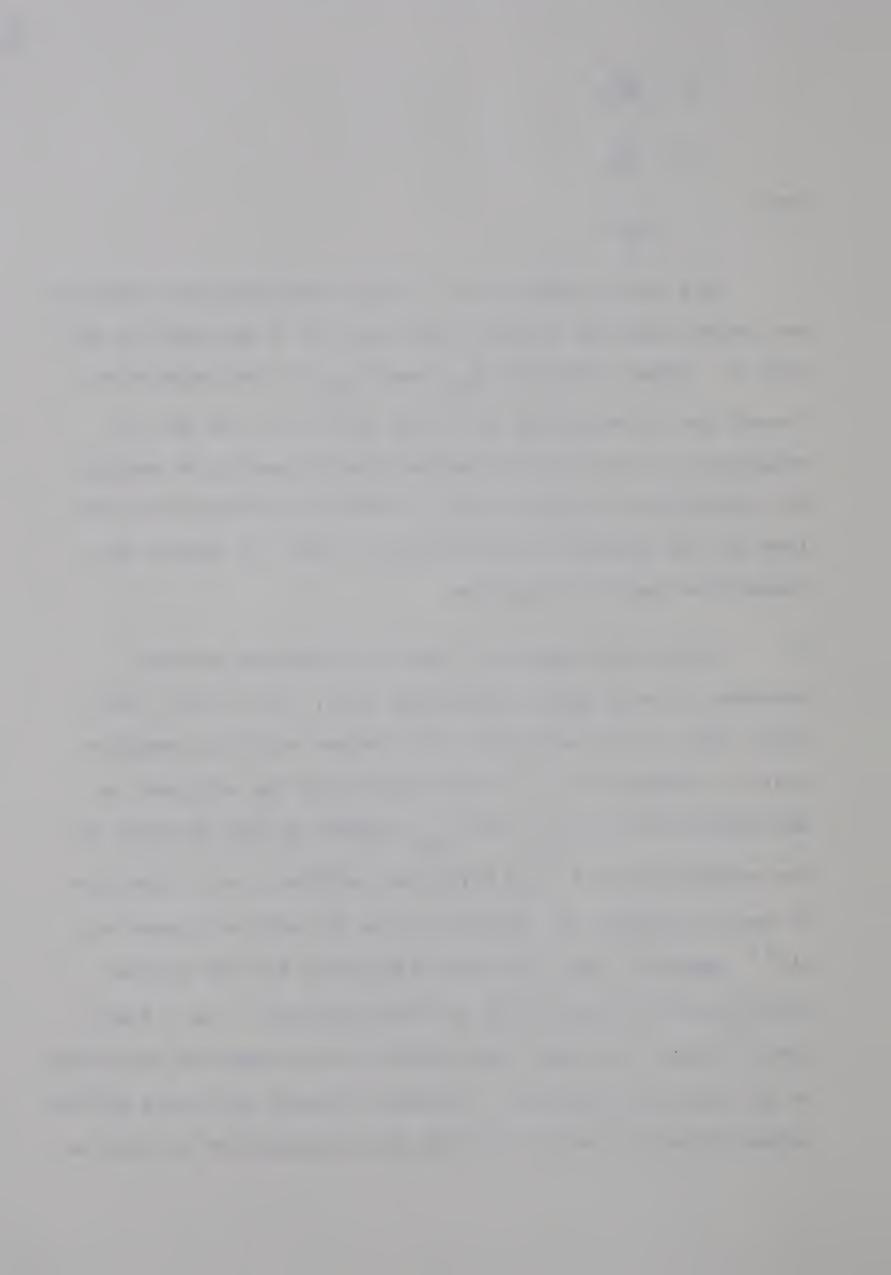
$$B = \frac{bP}{RT}$$

and

$$v = \frac{zRT}{P}$$

The cubic equation in z (the compressibility factor) was solved and the largest real value of z was used to obtain v. After replacing  $P_{H_2S}$  and  $P_{CO_2}$  by the respective fugacities in equations (9), (10) and (13), the set of equations (1) to (13) was solved simultaneously to obtain the fugacities of  $H_2S$  and  $CO_2$ . These fugacities were divided by the fugacity coefficients of each, to obtain the respective partial pressures.

b) In all the equations used to calculate partial pressure of acid gases (equations (14), (15), (17), (18), (20), (21), (22), and (23)) the average activity coefficient,  $\gamma$ , appears as  $\gamma^2$ . This means that the accuracy in the prediction of  $P_{CO_2}$  and  $P_{H_2S}$  depends on the accuracy in the prediction of  $\gamma$ . As mentioned earlier  $\gamma$  as a function of ionic strength was obtained from the work of Atwood et al. However, when the solubility data for the system  $CO_2-H_2S$ -water-EA were used to back-calculate  $\gamma$  as a function of ionic strength, the simple curves reported by Atwood et al. were not obtained. Instead a family of curves was obtained depending on the initial EA concentration as well as



temperature. Figure 8 shows  $\gamma$  as a function of ionic strength back-calculated from experimental data of Lee, Otto and Mather 15,16,17 and also of Leibush and Shneerson 23, for different temperatures and initial DEA concentrations. The thick line shows y as a function of ionic strength obtained from the work of Atwood et al. 1. As is evident from this figure,  $\gamma$  is not only a function of ionic strength, but is also a function of initial EA concentration and temperature. It can also be observed that  $\gamma$  decreases first and then increases as the concentration of ions in the solution increases (i.e. as ionic strength increases). With increasing initial EA concentration, the inflection point moves towards higher ionic strength. Theoretically this type of behavior is predicted by the Debye-Hückel Theory 5. From the figure it can also be observed that the temperature dependence of  $\gamma$  for the same initial EA concentration is small. In conclusion it can be said, by observing Figure 8, that the simple relationship of  $\gamma$  to ionic strength is inadequate. A correlation for  $\gamma$  which also incorporates the effects of temperature and initial EA concentration, is therefore, needed.

In this work an empirical function of temperature and initial EA concentration was added to the expression for  $\gamma$  vs ionic strength. The expression of  $\gamma$  can be written as:

$$\gamma = f_1 (\mu) + f_2 (T,m)$$
  $(X_{H_2}S + X_{CO_2}) > 0.2 \text{ moles/}$ 



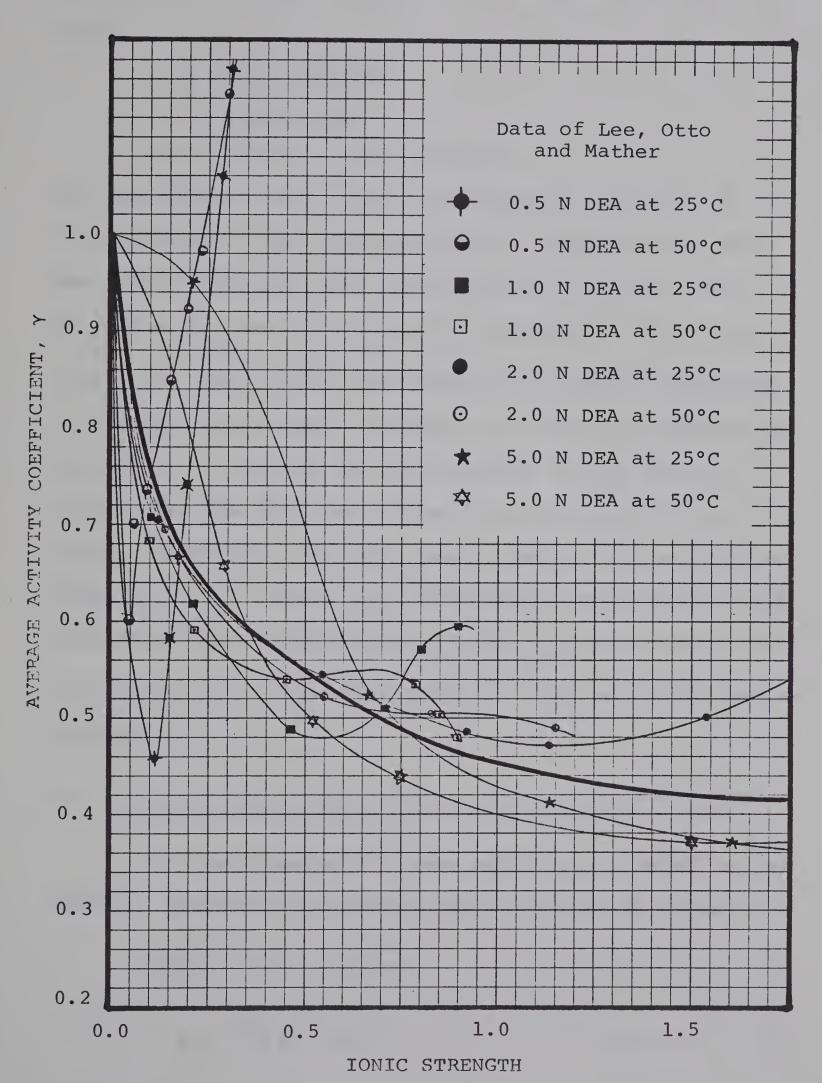


Figure 8 - Activity Coefficient vs Ionic Strength



$$\gamma = f_1 (\mu)$$
  $(X_{H_2S} + X_{CO_2}) < 0.2$  moles/mole of EA where:

 $\mu = ionic strength$ 

T = temperature

m = initial EA concentation.

The expressions for  $f_1$  and  $f_2$  are given in Appendix G. It was observed that the prediction of experimental data was not satisfactory with the empirical function, when  $X_{CO_2}$  plus  $X_{H_2S}$  was less than 0.2 moles/mole of EA. The reason for this is that the behavior of partial pressures of  $H_2S$  and  $CO_2$  is quite different at these low loadings of acid gases. Also the partial pressure of  $H_2S$  does not follow the same trend as the partial pressure of  $CO_2$  at these conditions. For this reason, empirical functions of temperature and initial EA concentration were added to the expressions for predicting  $P_{CO_2}$  and  $P_{H_2S}$  rather than to the expression for  $\gamma$ . The empirical functions are presented in Appendix G.

## C. The Correlation Based on Kent and Eisenberg Model:

Kent and Eisenberg<sup>10</sup> have used the following set of chemical equations to describe the H<sub>2</sub>S-water-EA system:

$$RR'NH_2^+ \stackrel{K_1}{\longleftarrow} H^+ + RR'NH \qquad ----- \qquad (1)$$

$$H_2O \stackrel{K_4}{\rightleftharpoons} H^+ + OH^-$$
 (4)



$$H_2S \stackrel{K_6}{\rightleftharpoons} H^+ + KS^-$$
 ---- (6)

$$HS^{-} \stackrel{K_{7}}{\rightleftharpoons} H^{+} + S^{2-}$$
 (7)

$$P_{H_2S} = H_{H_2S}[H_2S]$$
 ----- (9)

To describe the CO<sub>2</sub>-water-EA system the equations used are:

$$RR'NH_2^+ \stackrel{K_1}{\rightleftharpoons} H^+ + RR'NH \qquad ----- (1)$$

$$RR'NCOO \stackrel{K_2}{\longleftarrow} RR'NH + HCO_3 \qquad ----- (2)$$

$$H_2O+CO_2 \stackrel{K_3}{\rightleftharpoons} H^+ + HCO_3^-$$
 ----- (3)

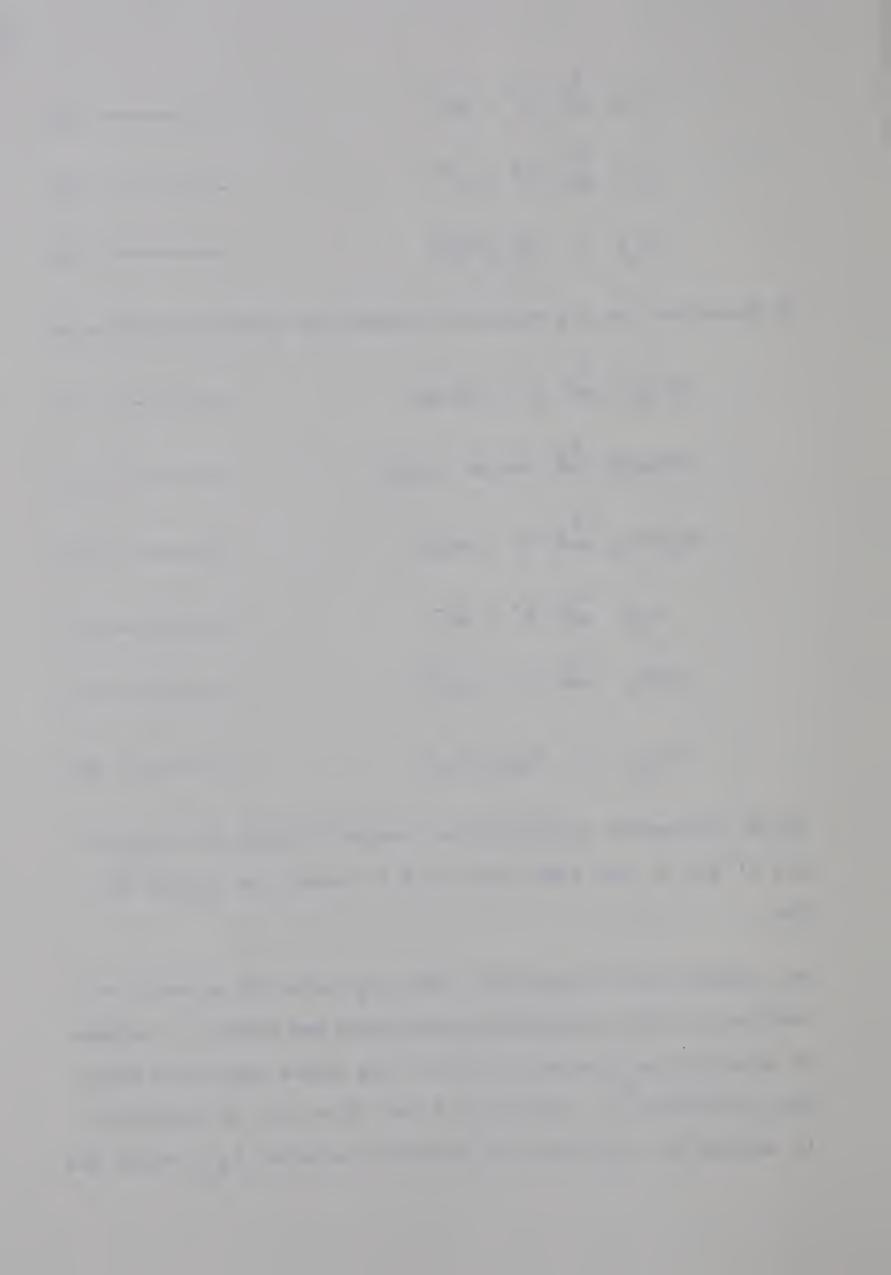
$$H_2O \stackrel{K_4}{\rightleftharpoons} H^+ + OH^- \qquad ----- (4)$$

$$HCO_3^- \xrightarrow{K_5} H^+ + CO_3^{2-}$$
 ---- (5)

$$P_{CO_2} = H_{CO_2}[CO_2]$$
 ----- (8)

RR'NH represents ethanolamine, where R stands for  $C_2^H_4^OH$  and R' for H, for MEA; and R and R' stand for  $C_2^H_4^OH$  for DEA.

The second set of equations (for  ${\rm CO_2}$ -water-EA system) is similar to that proposed by Danckwerts and McNeil<sup>4</sup>. Values of equilibrium constants for all the above equations have been published<sup>10</sup>. However, if the first set of equations is solved for  ${\rm H_2S}$ -water-EA system to predict  ${\rm P_{H_2S}}$  using the



published equilibrium constants, an unsatisfactory fit of the published vapor data results<sup>10</sup>. Similarly if the second set of equations for CO<sub>2</sub>-water-EA system is solved for P<sub>CO<sub>2</sub></sub>

an unsatisfactory fit of the experimental data results. solve this problem, Kent and Eisenberg 10, treated the equilibrium constant  $K_1$ , representing the EA reaction (for the system H<sub>2</sub>S-water-EA), as a variable and accepted all the remaining equilibrium constants as published. Using published vapor pressure data for 15.3 weight percent MEA solution and 20.5 weight percent DEA solution, those values for K<sub>1</sub> which fit the data were found for each temperature. For CO2-water-EA system an additional equilibrium constant, K2, was used because CO2 is capable of reacting directly with either MEA or DEA to form the amine salt of a substituted carbamic acid (the carbamate ion). To solve this set of equations, only K2 was allowed to vary. For the ionic dissociation reactions, values from the literature were For K<sub>1</sub>, the value found for the H<sub>2</sub>S-water-EA system was used. Both K<sub>1</sub> and K<sub>2</sub> show an Arrhenius dependency on temperature 10.

All the above equations were combined into a model for the mixed system, i.e. the system containing both CO<sub>2</sub> and H<sub>2</sub>S in aqueous EA solution. From equations (1) to (9) the following expressions for the pseudo-equilibrium constants can be written:



$$K_1 = \frac{[H^+][RR'NH]}{[RR'NH_2^+]}$$
 ----- (i)

$$K_2 = \frac{[RR'NH][HCO_3]}{[RR'NCOO]}$$
 ----- (ii)

$$K_3 = \frac{[H^+][HCO_3]}{[CO_2]}$$
 ----- (iii)

$$K_4 = [H^+][OH^-]$$
 ----- (iv)

$$K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$
 ----- (v)

$$K_6 = \frac{[H^+][HS^-]}{[H_2S]}$$
 ----- (vi)

$$K_7 = \frac{[H^+][S^{2-}]}{[HS^-]}$$
 ----- (vii)

$$H_{CO_2} = \frac{P_{CO_2}}{[CO_2]} \qquad ----- \text{(viii)}$$

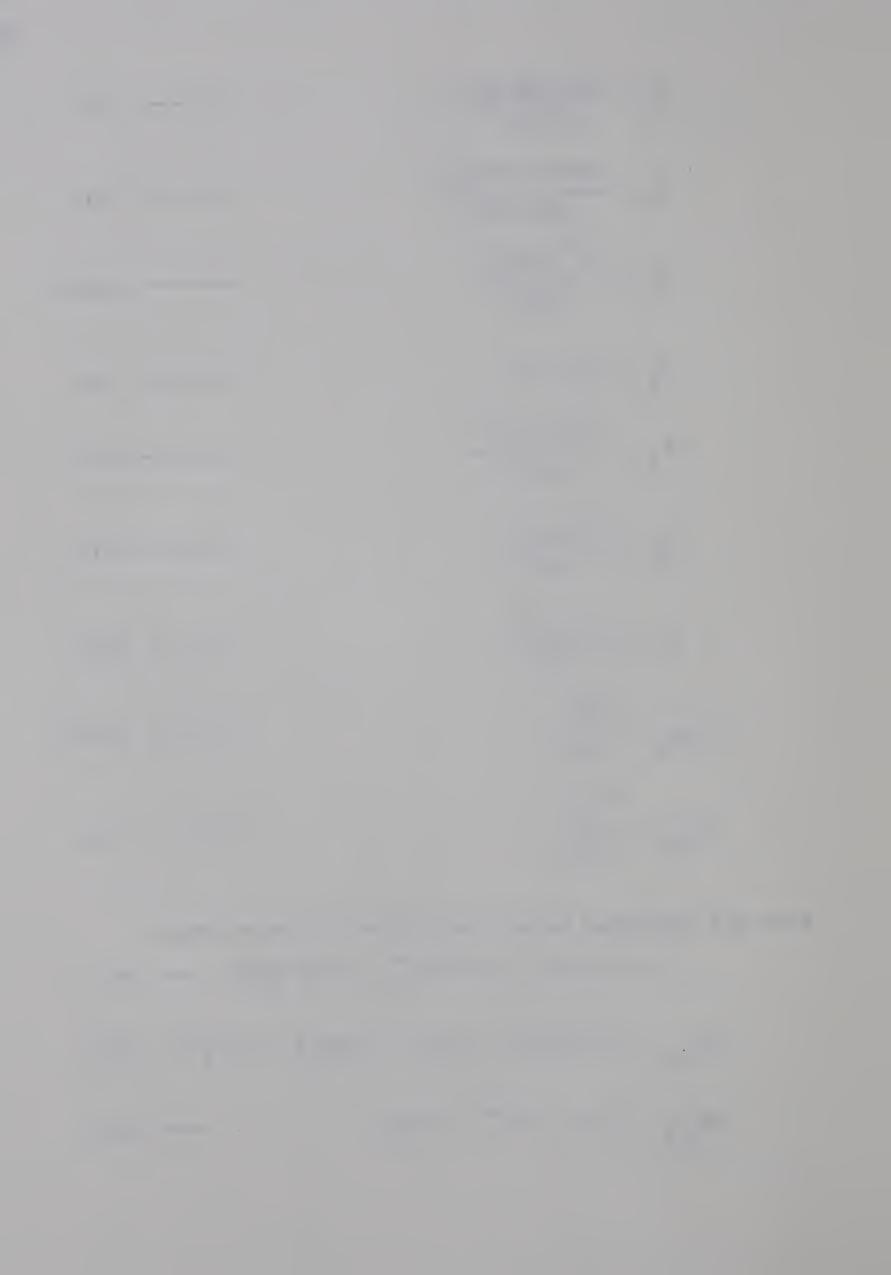
$$H_{H_2S} = \frac{P_{H_2S}}{[H_2S]}$$
 ----- (ix)

Also the following balance equations can be written:

$$m = [RR'NH] + [RR'NH_2^+] + [RR'NCOO] ---- (x)$$

$$mX_{CO_2} = [R'RNCOO] + [CO_2] + [HCO_3] + [CO_3^{2-}] (xi)$$

$$mX_{H_2S} = [HS^-] + [S^{2-}] + [H_2S]$$
 ---- (xii)



$$[RR'NH_2^+] + [H^+] = [HCO_3^-] + [RR'NCO_0^-] + 2[CO_3^{2-}]$$
  
+ 2[S\_] + [OH\_] + [HS\_]

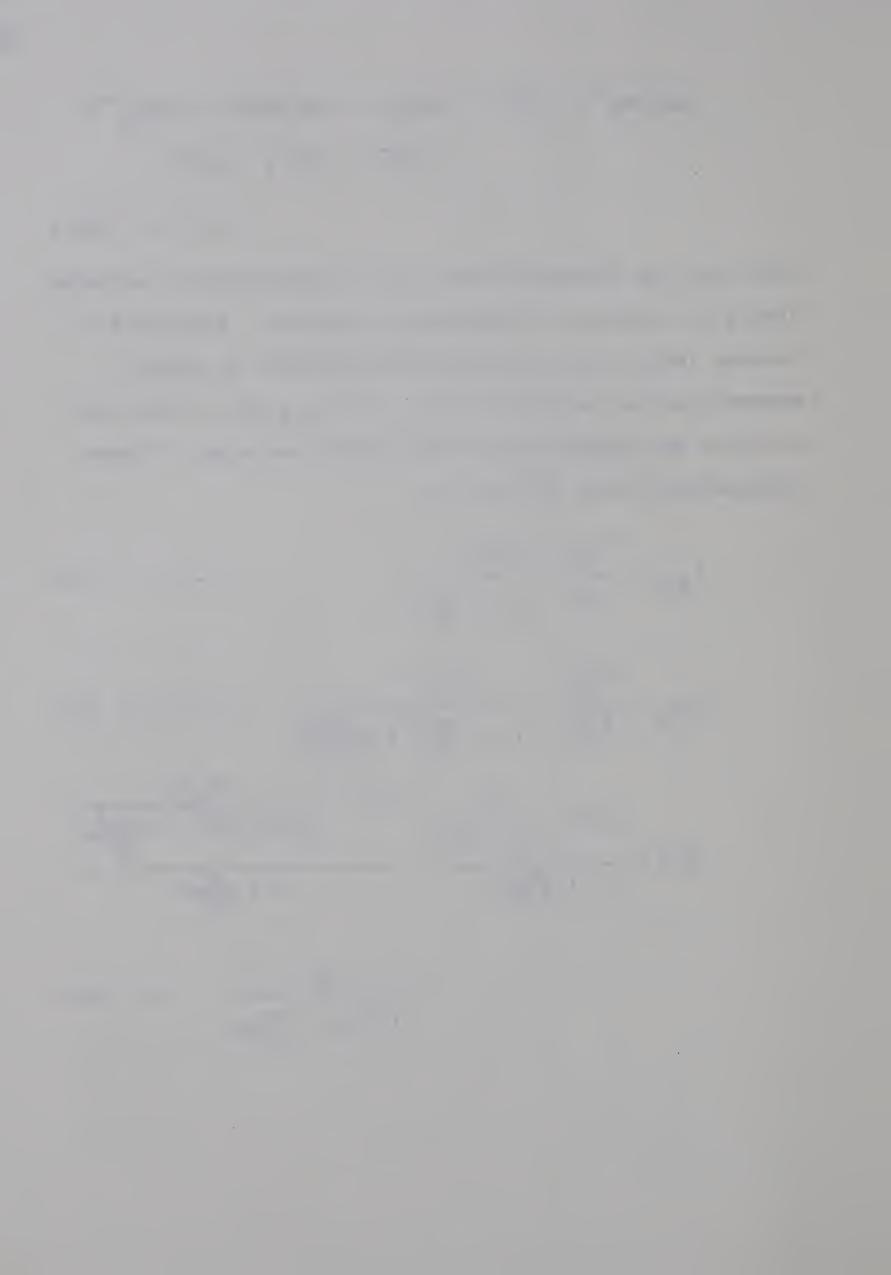
where all the concentrations are in moles/liter of solution. Also m is in moles of EA/liter of solution. Equations (i) through (xiii) can be solved simultaneously to obtain expressions for calculating  $P_{CO_2}$  and  $P_{H_2S}$  when liquid composition and temperature of the system are known. These expressions can be written as:

$$P_{H_2S} = \frac{H_{H_2S}}{K_6K_7} \cdot \frac{A[H^+]^2}{(1 + \frac{[H^+]}{K_7})}$$
 ----- (14)

$$P_{CO_2} = \frac{{}^{H}_{CO_2}}{{}^{K_3}{}^{K_5}} \cdot \frac{{}^{B[H^+]^2}}{(1 + \frac{[H^+]}{K_5} + \frac{m[H^+]}{K_2 K_5 K'})} ----- (15)$$

$$[H^{+}] = \frac{\frac{K_{7}}{K_{7} + [H^{+}]}}{\frac{(1 + \frac{m}{K_{1}K^{*}})}{(1 + \frac{m}{K_{1}K^{*}})}} + \frac{\frac{K_{2}K_{5}}{K_{2}K_{5} + K_{2}[H^{+}] + \frac{m[H^{+}]}{K^{*}}}}{\frac{(1 + \frac{m}{K_{1}K^{*}})}{(1 + \frac{m}{K_{1}K^{*}})}}$$

$$+ \frac{K_4}{[H^+](1 + \frac{m}{K_1 K'})} \qquad ---- (16)$$



where

$$A = X_{H_2S}^m - \frac{P_{H_2S}}{H_{H_2S}}$$

$$B = X_{CO_2}^m - \frac{P_{CO_2}}{H_{CO_2}}$$

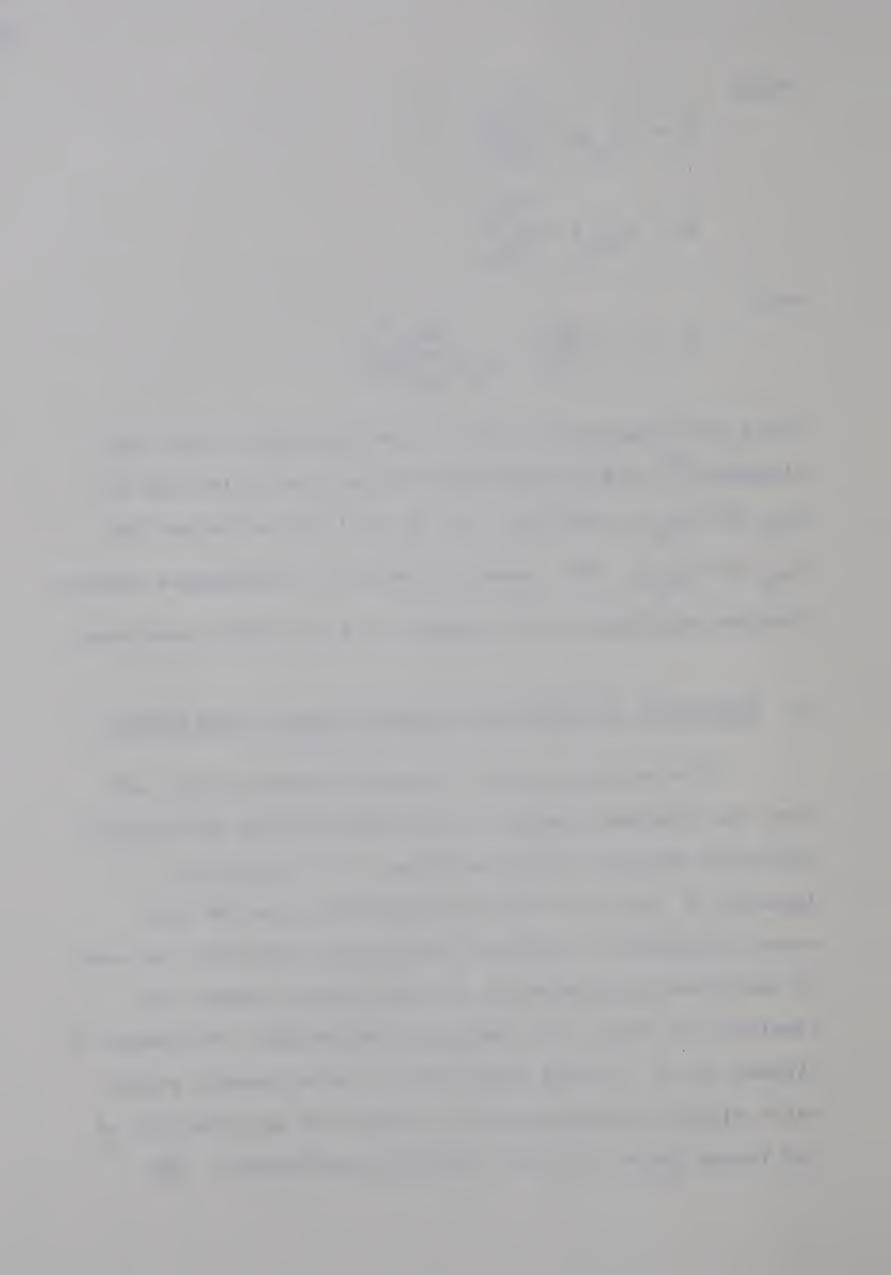
and

$$K' = 1 + \frac{[H^+]}{K_1} + \frac{P_{CO_2} K_3}{K_2 H_{CO_2} [H^+]}$$

Using the values of  $K_1$  and  $K_2$  from the work of Kent and Eisenberg<sup>10</sup>, and the published values for  $K_3$  through  $K_7$ ,  $H_{CO_2}$  and  $H_{H_2S}$ , equations (14) to (16) can be solved for  $P_{CO_2}$  and  $P_{H_2S}$ . The numerical method of successive approximations was found to be adequate to solve these equations.

## D. Comparison of Predictive Capabilities of the Models:

The starting point, for both Klyamer et al. and Kent and Eisenberg models, is the postulation of chemical reactions occuring in the solution. It is shown in Appendix D that for the system H<sub>2</sub>S-CO<sub>2</sub>-water-EA only seven independent reactions are possible and that the sets of reactions postulated in the two models, though not identical in form, are chemically equivalent. The model of Klyamer et al. is more sound from a thermodynamic standpoint since it incorporates the effect of non-ideality of the liquid phase by using activity coefficients. The



substitution of partial pressure by fugacity, in the modified form of this model, lends it more theoretical support at higher pressures. The inclusion of fugacity takes care of the non-ideality of the gas phase. The model of Kent and Eisenberg incorporates all the non-idealities into two parameters, namely  $K_1$  and  $K_2$ . This changes the nature of  $K_1$  and  $K_2$  from equilibrium constants to two empirical parameters which enable the model to fit the experimental data better.

The following generalizations can be made about the prediction capabilities of the three models (namely, Klyamer et al., Kent and Eisenberg and Modified Klyamer et al.) by observing Figures 9 to 26 in Appendix E:

(i) In general for MEA, the model of Klyamer et al. predicts lower values of  $P_{H_2S}$  and  $P_{CO_2}$  (compared to the experimental ones), for  $X_{CO_2}$  plus  $X_{H_2S}$  greater than ca. 0.3 moles/mole of EA. For loadings lower than 0.3 moles/mole of EA, values of  $P_{H_2S}$  and  $P_{CO_2}$  higher than the experimental ones are predicted. The prediction worsens with increasing EA concentration and acid gas loadings. For DEA, the prediction of  $P_{H_2S}$  and  $P_{CO_2}$  is, in general, better than that for MEA.



- (ii) Only for simple systems, i.e. systems containing either  ${\rm CO_2}$  or  ${\rm H_2S}$ , the data fit obtained by Kent and Eisenberg model is fairly good. For mixtures  $({\rm H_2S-CO_2-water-EA}$  system), on the other hand, prediction of  ${\rm P_{CO_2}}$  and  ${\rm P_{H_2S}}$  worsens with increasing EA concentration: increasing loadings of  ${\rm CO_2}$  and  ${\rm H_2S}$ ; and decreasing temperature.
- (iii) The modified Klyamer et al. model predicts experimental data reasonably well over most conditions of temperature and EA concentrations, when both acid gases are present. For aqueous MEA solution containing either  ${\rm CO_2}$  or  ${\rm H_2S}$ , the predicted  ${\rm P_{H_2S}}$  and  ${\rm P_{CO_2}}$  values are, in general, higher than the experimental ones. For DEA, when  ${\rm X_{CO_2}}$  or  ${\rm X_{H_2S}}$  is less than 0.4 moles/mole of EA, the predicted values of  ${\rm P_{CO_2}}$  and  ${\rm P_{H_2S}}$  are usually slightly higher than the experimental values. However, for loadings greater than 0.4 moles (of  ${\rm CO_2}$  or  ${\rm H_2S}$ )/mole of EA, the fit is reasonably good. When both  ${\rm X_{H_2S}}$  and  ${\rm X_{CO_2}}$  are less than 0.1 mole/mole of EA, this model reproduces the trend, followed by experimental  ${\rm P_{H_2S}}$  and  ${\rm P_{CO_2}}$  values, however, deviation in some regions is still present.

By comparing the predictions of each of the three models with the experimental data, the following conclusions can be drawn:



- (1) For simple systems only, i.e. systems containing either  ${\rm CO_2}$  or  ${\rm H_2S}$ , the model of Kent and Eisenberg reproduces the experimental data best, over most conditions of temperature, EA concentrations and acid gas loadings. For the same systems, in most cases Klyamer et al. model also gives a reasonable fit. Modified Klyamer et al. model, on the other hand, usually predicts slightly higher  ${\rm P_{CO_2}}$  and  ${\rm P_{H_2S}}$  values, compared to the experimental ones.
- For mixtures of CO2 and H2S in aqueous solutions, (2) the Modified Klyamer et al. model fits the experimental data best, especially as temperature decreases; EA concentration increases; and as the loading of acid gases in-For loadings of CO, plus H,S greater than ca. 0.8 moles/mole of EA, the modified Klyamer et al. model predicts P<sub>CO2</sub> and P<sub>H2</sub>S which are slightly lower than experimental values, but are much better than predictions from the other two models. For DEA the Kent and Eisenberg model, though not better than modified model for mixtures, is better than the Klyamer et al. model in most cases. For MEA, both the Klyamer et al. and the Kent and Eisenberg, models give results which are in error by about the same order of magnitude. Tables I and II, summarize the above observations for the mixtures of CO2 and H2S in EA solutions. Each entry in the table gives the percent deviation



in the predicted partial pressure values as compared to the experimental ones. Models I, II, and III stand for Klyamer et al., Kent and Eisenberg and Modified Klyamer et al. models, respectively.

(3) Only the Modified Klyamer et al. model is able to reproduce the trend of sharply declining  $P_{H_2S}$  and  $P_{CO_2}$  for low acid gas loadings (when both  $X_{CO_2}$  and  $X_{H_2S}$  are less than 0.1 moles/mole of EA).



\*

\*\*\*

PERCENT DEVIATION IN PREDICTION OF PARTIAL PRESSURES TABLE I:

					8 DEVIATION	TION		•
AMINE	AMINE	PARTIAL		100 °C			40 °C	,
	CONCENTRATIONS	PRESSURES	MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL DE
	, c	P <sub>H2</sub> S	-70	-50	-15	-100	06-	+7
K		Pco2	L-	-10	+27	-40	06-	+30
	c Z	P <sub>H2</sub> S	-120	-130	-48	06-	-140	-4
		Pco <sub>2</sub>	-100	-190	-53	-13	-130	+23
				100 °C			2° 05	
			MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
	2	P <sub>H2</sub> S	6-	0	+20	-94	-35	0
. 6	2	Pco <sub>2</sub>	-20	-12	+3	-124	-83	-14
4	z v	P <sub>H2</sub> S	-18	-13	+19	-67	-26	+20
		Pco <sub>2</sub>	-80	-80	-34	- 65	-50	+19

Percent Deviation = - (P) Fredicted - (P) Experimental (P) predicted \*\*\*

 $x_{H_2}s = x_{CO_2} = 0.4$  moles/mole of EA



\*
PERCENT DEVIATION IN PREDICTION OF PARTIAL PRESSURES\* TABLE II:

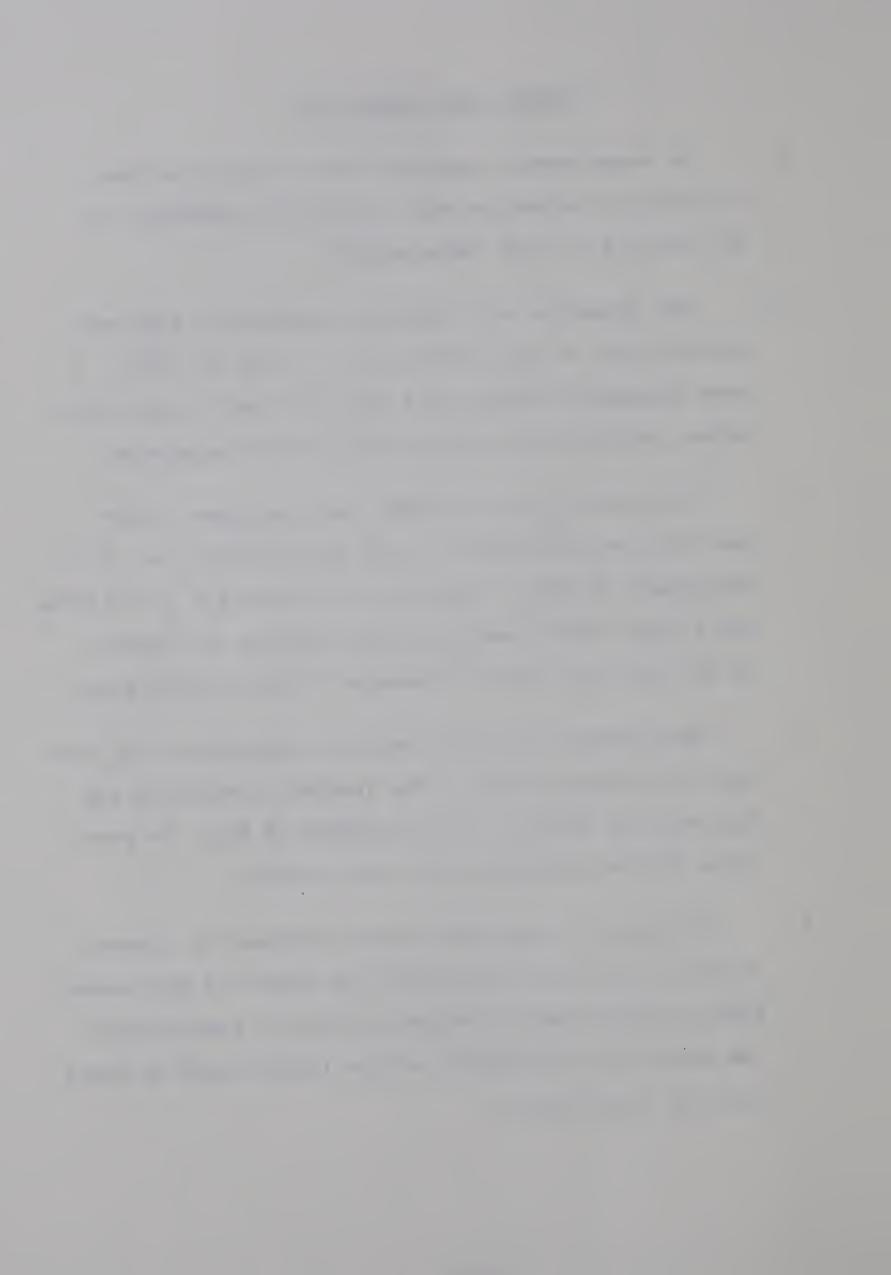
AMINE CONCENTRATIONS . MEA . MEA . 5.0 N	PARTIAL						
	rkessones		100 °C			40 °C	
		MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
	P <sub>H2</sub> S	-13	-25	+10	-11	-31	+10
	Pco <sub>2</sub>	L-	-35	+27	*	*	*
	P <sub>H2</sub> S	-80	-80	-27	-14	-36	+14
	Pco <sub>2</sub>	-38	-67	0	*	*	*
			100 °C			၁ <sub>°</sub> 05	
		MODEL I	MODEL II	MODEL III	MODEL I	MODEL II	MODEL III
	P <sub>H2</sub> S	9-	0	+13	-14	0	+22
	Pco <sub>2</sub>	6-	9+	+10	-26	-31	8 +
2 "	P <sub>H2</sub> S	0.	+15	+21	-34	0	+17
	P <sub>CO2</sub>	-62	-13	-23	-61	-31	0

\*\* No experimental data available \* X<sub>H S</sub> = X<sub>CO</sub> = 0.2 moles/mole of EA

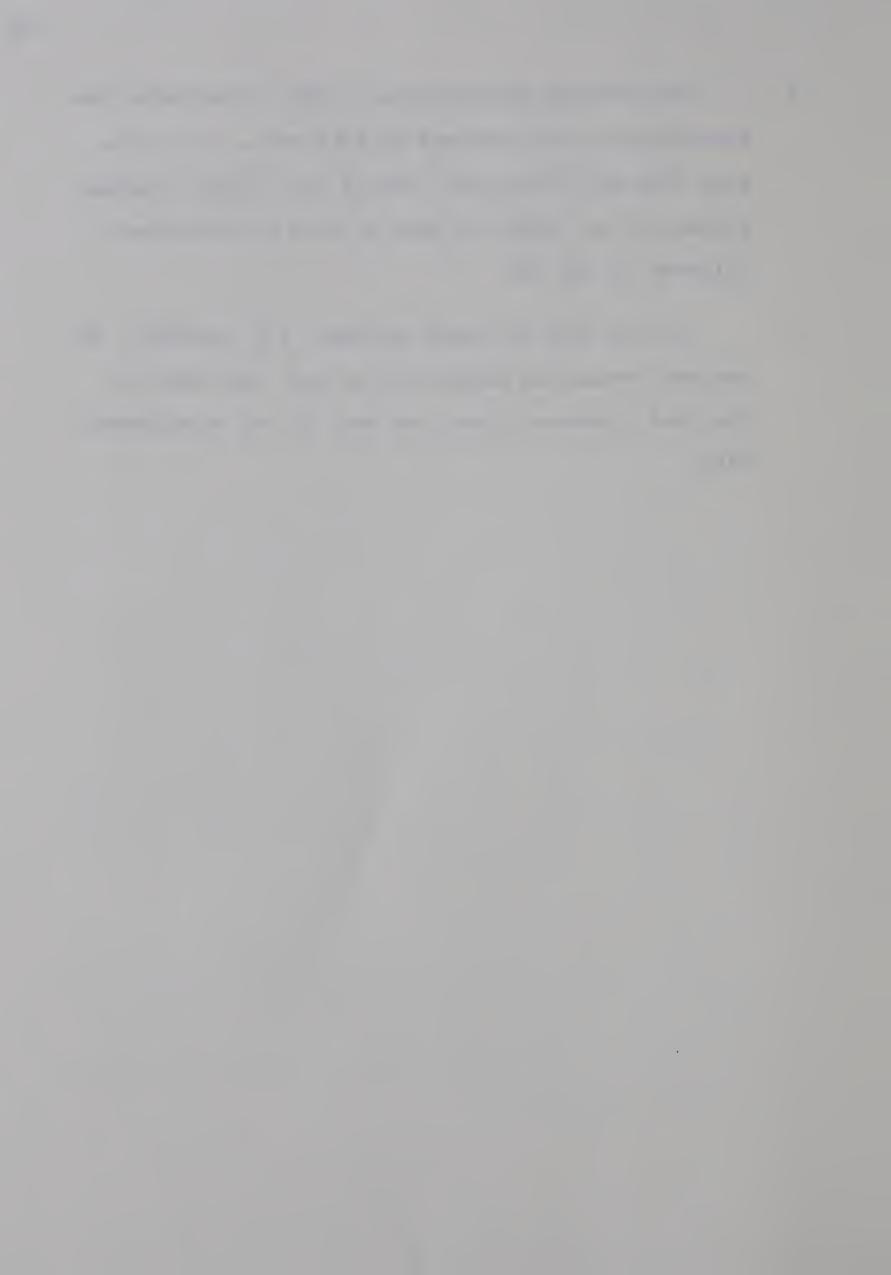


### SUMMARY AND CONCLUSIONS

- 1. An experimental apparatus was designed and constructed to determine very low partial pressures of  ${\rm CO}_2$  and  ${\rm H}_2{\rm S}$  at high temperatures.
- 2. The apparatus was tested by reproducing some solubility data of H<sub>2</sub>S and CO<sub>2</sub> in 2.5 N MEA at 100°C. A good agreement between this data and that in the literature, confirmed the reliability of this apparatus.
- 3. For pure CO<sub>2</sub> in 2.5 N MEA, two isotherms at 80° and 100°C were extended to very low loadings (ca. 0.02 moles/mole of MEA). Similarly, for pure H<sub>2</sub>S in 2.5 N MEA the 80° and 100°C isotherms were extended to regions of very low H<sub>2</sub>S partial pressures. (about 0.0004 psia)
- 4. Measurements were also made for mixtures of CO<sub>2</sub> and H<sub>2</sub>S in 5 N MEA at 100°C. The loading of each CO<sub>2</sub> and H<sub>2</sub>S was less than ca. 0.1 moles/mole of MEA. No previous data were available for this region.
- of the two theoretical models proposed by Klyamer et al. and Kent and Eisenberg, the former is more sound from a thermodynamic standpoint since it incorporates the effect of non-ideality of the liquid phase by using activity coefficients.

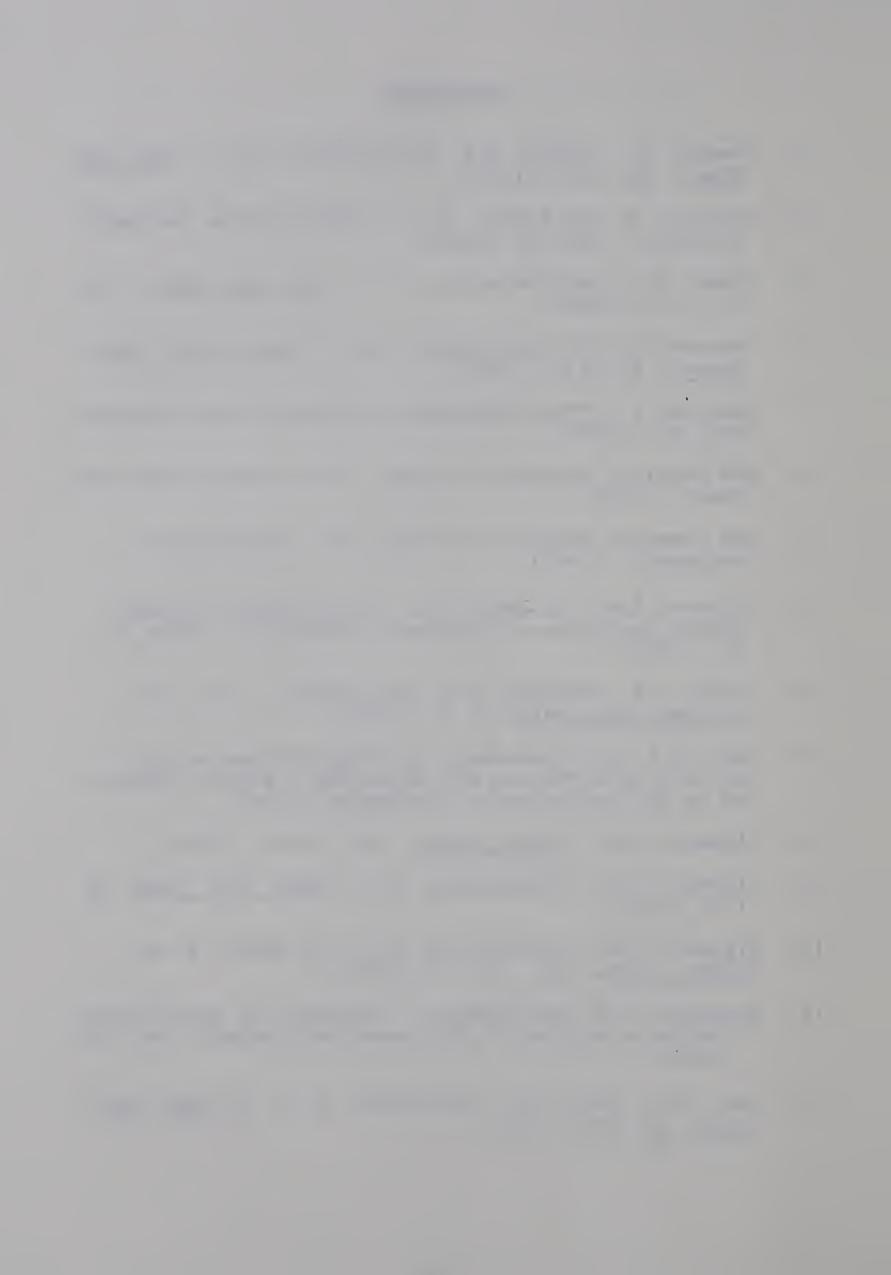


- 6. The modified Klyamer et al. model, reproduces the experimental data obtained in this work, as well as that from the literature, better than either original Klyamer et al. model or that of Kent and Eisenberg. (Figures 25 and 26).
- 7. For the case of simple systems, i.e. aqueous EA systems containing either CO<sub>2</sub> or H<sub>2</sub>S, the model of Kent and Eisenberg gives the best fit of experimental data.



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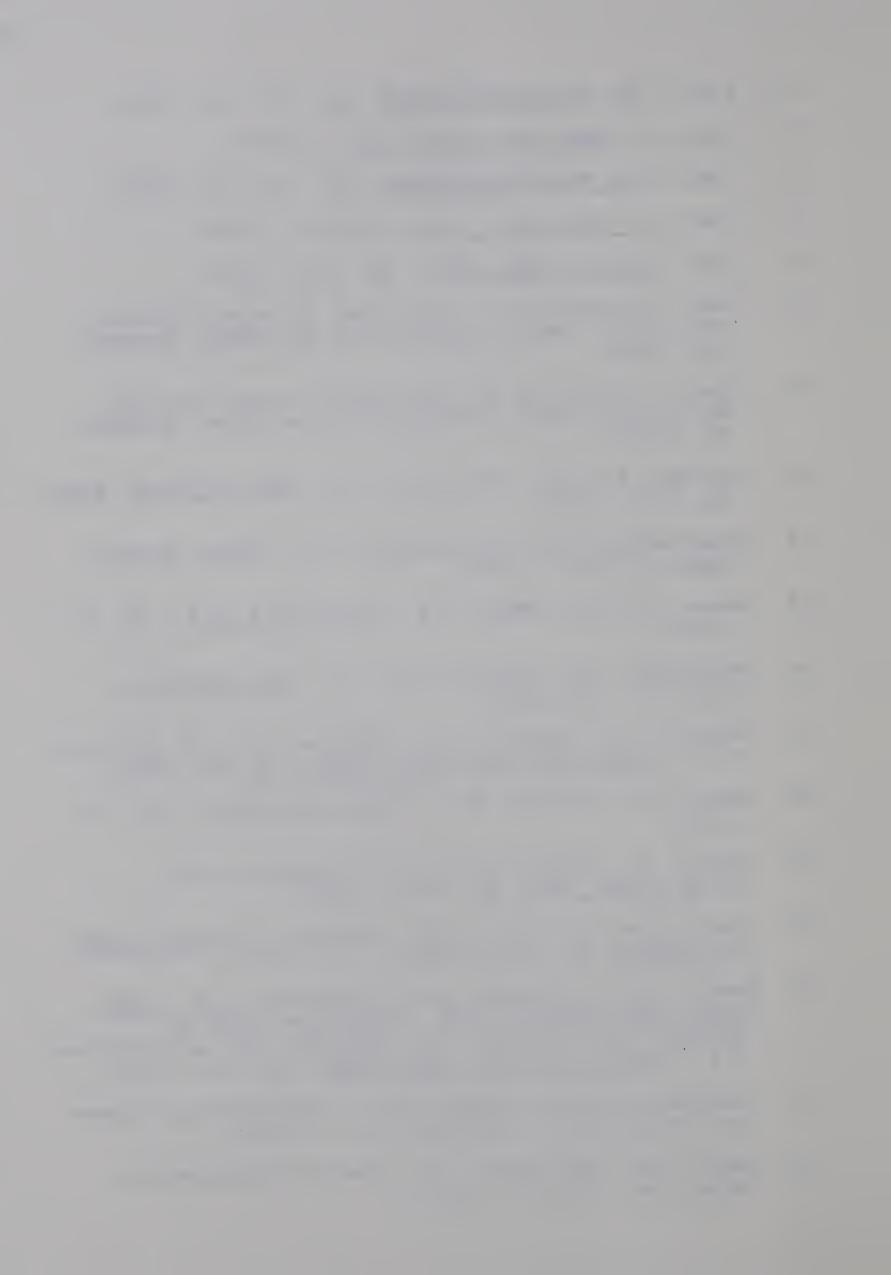
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# APPENDIX A

CALCULATION OF P<sub>H2</sub>S' P<sub>CO2</sub>' ETHANOLAMINE NORMALITY, X<sub>H2</sub>S and X<sub>CO2</sub>.



### Calculations

### a) Gas Phase:

Peak area for each gas,  $N_2$ ,  $CO_2$  and  $H_2S$  was divided by its Relative Molar Response (RMR) factor. Mole percent of each acid gas was obtained by the formula:

Mole percent H<sub>2</sub>S =

$$\frac{\frac{\text{Peak Area H}_2\text{S}}{(\text{RMR})_{\text{H}_2}\text{S}}}{\times 100} \times 100$$

$$\frac{\text{Peak Area H}_2\text{S}}{(\text{RMR})_{\text{H}_2}\text{S}} + \frac{\text{Peak Area CO}_2}{(\text{RMR})_{\text{CO}_2}} + \frac{\text{Peak Area N}_2}{(\text{RMR})_{\text{N}_2}}$$

Similarly,

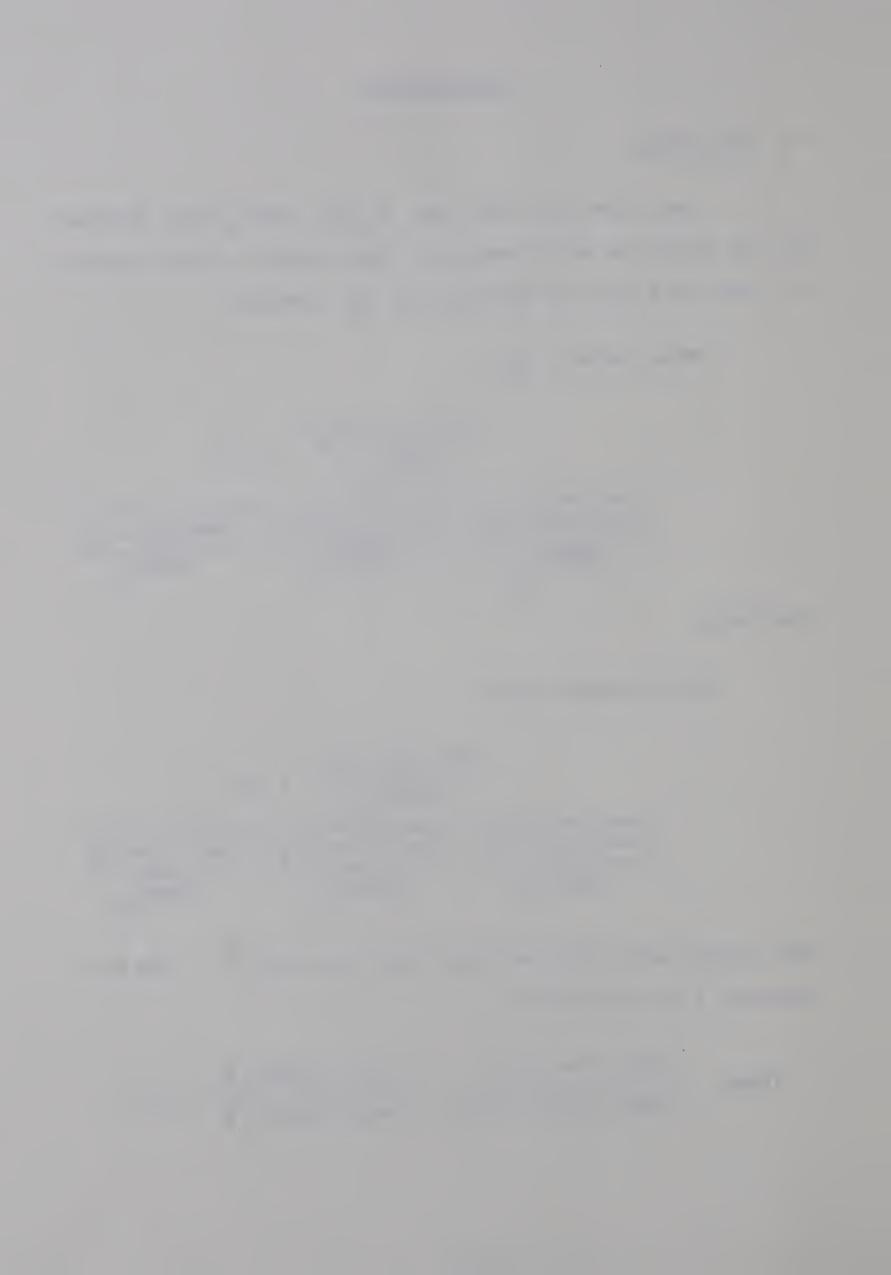
Mole percent CO<sub>2</sub>=

$$\frac{\text{Peak Area CO}_2}{(\text{RMR})_{\text{H}_2}\text{S}} \times 100$$

$$\frac{\text{Peak Area H}_2\text{S}}{(\text{RMR})_{\text{H}_2}\text{S}} + \frac{\text{Peak Area CO}_2}{(\text{RMR})_{\text{CO}_2}} + \frac{\text{Peak Area N}_2}{(\text{RMR})_{\text{N}_2}}$$

RMR factors were obtained from the literature  $^{30}$ . RMR for compound i is defined as:

$$(RMR)_{i} = \frac{Peak \text{ area of } i}{mole \text{ percent of } i} \times \frac{mole \text{ percent } \phi}{Peak \text{ area of } \phi} \times 100$$



where  $\phi$  refers to the internal standard (benzene) and the factor 100 represents the RMR of benzene arbitrarily assigned a response of 100 units per mole<sup>30</sup>.

Since the total pressure was always near atmospheric and since the temperature was reasonably high, an ideal gas phase was assumed in calculating the partial pressures of  $H_2S$  and  $CO_2$ . Vapor pressure of water plus amine was subtracted from the absolute pressure in B-3 to obtain the pressure due to  $N_2$ ,  $CO_2$  and  $H_2S$ , designated as

$$\bar{P}(N_2 + H_2S + CO_2)$$
.

Then:

Partial Pressure of 
$$H_2S$$
,  $P_{H_2S}$ 

$$= \frac{\text{Mole percent } H_2S}{100} \times \bar{P}(N_2 + CO_2 + H_2S)$$

Similarly,

= Partial Pressure of CO<sub>2</sub>, P<sub>CO<sub>2</sub></sub>

$$= \frac{\text{Mole percent CO}_2}{100} \times \bar{P}(N_2 + CO_2 + H_2S)$$

# b) Liquid Phase:

Normality of amine (MEA), N<sub>MEA</sub>:

 $N_{\mbox{MEA}} = \frac{\mbox{ml. of sulphuric acid used x normality of the acid}}{\mbox{ml. of sample used}}$ 

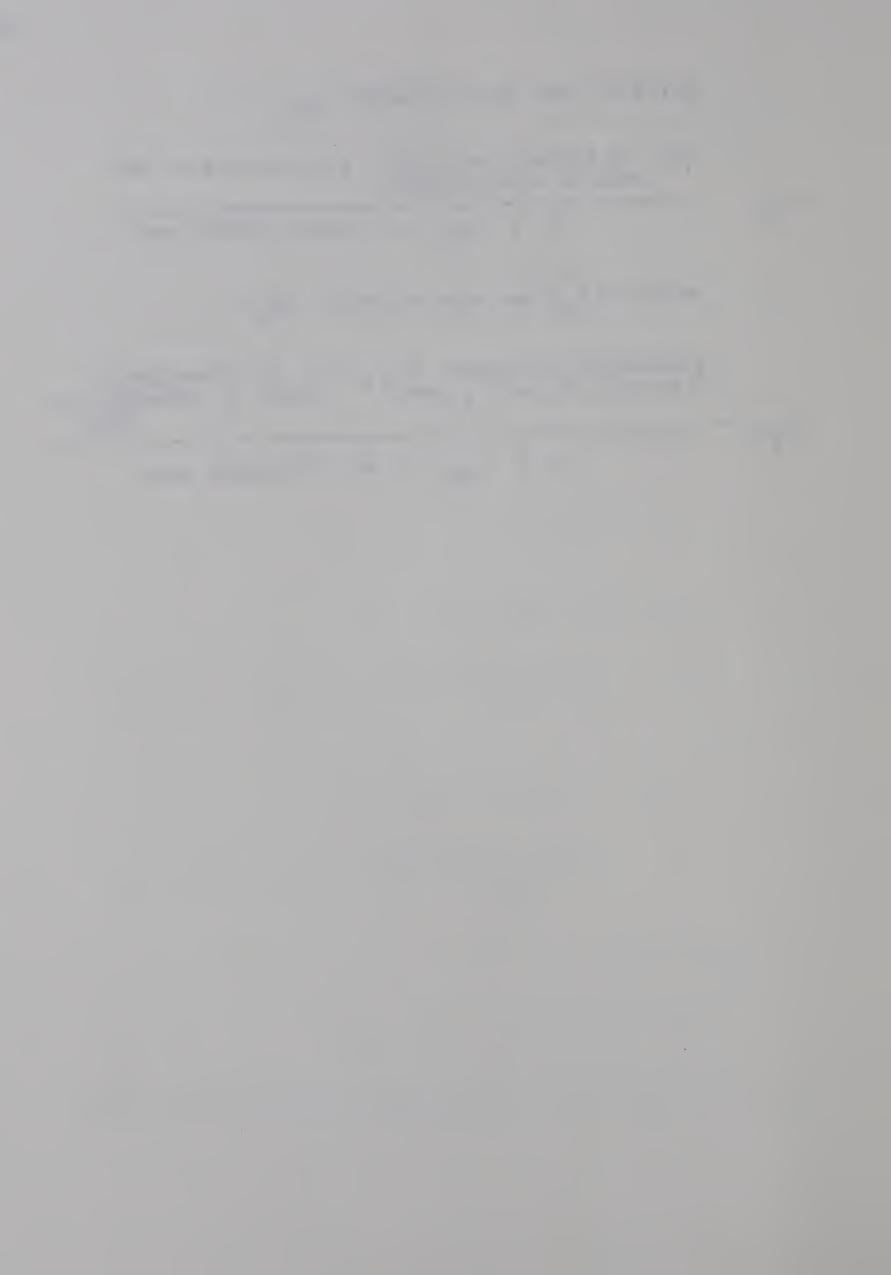


Moles CO<sub>2</sub> per mole of amine, X<sub>CO<sub>2</sub></sub>:

 $x_{CO_2} = \frac{\text{ml. of hydrochloric acid } x \text{ normality of HCl}}{2 \text{ x N}_{MEA} \text{ x ml. of sample used}}$ 

Moles of H<sub>2</sub>S per mole of amine, X<sub>H<sub>2</sub>S</sub>:

 $X_{\text{H}_2S} = \frac{\left( \text{Normality of Iodine x } \right) - \left( \text{ml. of thiosulphate used} \right)}{2 \times N_{\text{MEA}}} \times \text{ml. of sample used}$ 



### APPENDIX B

### EXPERIMENTAL RAW DATA

- a) Experimental Data for the Solubility of CO<sub>2</sub> in MEA Solutions.
- b) Experimental Data for the Solubility of H<sub>2</sub>S in MEA Solutions.
- c) Solubility of H<sub>2</sub>S-CO<sub>2</sub> Mixtures in
  5 N MEA Solution at 100°C.



# (a) Experimental Data for the Solubility of CO<sub>2</sub> in MEA Solutions:

# (i) 2.5 N MEA Solution

T/°C	P <sub>CO<sub>2</sub></sub> (Psia)	X <sub>CO<sub>2</sub></sub> (moles CO <sub>2</sub> /mole MEA)
60	0.0113 0.012 0.013	0.195 0.194 0.22
80	0.0017 0.00176 0.0022 0.003 0.0027 0.0097 0.0149 0.0126 0.028 0.033 0.067 0.071 0.072 0.081	0.031 0.0313 0.0325 0.052 0.093 0.112 0.115 0.158 0.161 0.214 0.220 0.217 0.226
100	0.00017 0.0002 0.0005 0.00053 0.00063 0.00067 0.00076 0.00098 0.0010 0.0052 0.0135 0.0141 0.023 0.109	0.0276 0.0275 0.029 0.031 0.0312 0.028 0.036 0.035 0.033 0.0573 0.080 0.082 0.094 0.143



## (ii) 5.0 N MEA Solution

T/°C	P <sub>CO<sub>2</sub></sub> (Psia)	X <sub>CO<sub>2</sub></sub> (Mole CO <sub>2</sub> /mole MEA)
100	0.00034 0.00053 0.00077 0.0042 0.0081 0.016 0.043 0.054 0.130	0.035 0.0375 0.039 0.060 0.067 0.076 0.087 0.087
	0.190	0.148

(b) Experimental Data for the Solubility of H<sub>2</sub>S in MEA Solutions:

# (i) 2.5 N MEA Solution

T/°C	P <sub>H2</sub> S (Psia)	X <sub>H2</sub> S (Mole	H <sub>2</sub> S/mole MEA)
80	0.00483 0.0052 0.011 0.011 0.0166 0.0172 0.023	0.028 0.027 0.041 0.042 0.046 0.0465 0.055	
	0.025 0.05 0.065 0.079 0.081 0.085 0.162	0.055 0.066 0.078 0.078 0.097 0.089 0.148	



T/°C	P <sub>H2</sub> S (Psia)	X <sub>H2</sub> S (Mole H <sub>2</sub> S/mole MEA)
100	0.0007 0.0012 0.0033 0.0081 0.0164 0.062 0.068 0.062	0.012 0.017 0.017 0.0216 0.0294 0.053 0.048 0.053

# (ii) 5.0 N MEA Solution:

100	0.00031	0.026
	0.0051	0.0344
	0.0097	0.0303
	0.0156	0.029
	0.040	0.037
	0.055	0.0435

(c) Solubility of H<sub>2</sub>S-CO<sub>2</sub> Mixtures in 5.0 N MEA Solution at 100°C. (Partial Pressures in Psia; X, Mole of acid gas/mole MEA).

P <sub>H2</sub> S	P <sub>CO2</sub>	X <sub>H2</sub> S	<sup>X</sup> co <sub>2</sub>
0.0019 0.0022 0.0066 0.026 0.047 0.054 0.077 0.085 0.097 0.102 0.118 0.13 0.15 0.16	0.0015 0.0029 0.0088 0.00031 0.0024 0.0038 0.071 0.097 0.0021 0.048 0.164 0.063 0.0094 0.0013 0.088	0.013 0.0083 0.010 0.0264 0.025 0.0463 0.0133 0.013 0.036 0.018 0.011 0.021 0.032 0.042 0.042	0.0405 0.0475 0.072 0.009 0.026 0.023 0.096 0.119 0.012 0.078 0.116 0.082 0.028 0.028 0.006
0.197 0.256	0.056 0.00354	0.033 0.053	0.06 0.012



PH <sub>2</sub> S	Pco <sub>2</sub>	X <sub>H2</sub> S	Xco <sub>2</sub>
0.305 0.44 0.46 0.47 0.490 0.557 0.60 0.61 0.64 0.64 0.653 0.716 0.76 0.93 0.988 1.04 1.056 1.11 1.29	0.175 0.002 0.13 0.028 0.123 0.115 0.004 0.033 0.038 0.01 0.015 0.015 0.0132 0.04 0.16 0.07 0.17 0.069 0.006 0.0082	0.022 0.06 0.035 0.053 0.046 0.037 0.084 0.066 0.063 0.08 0.0796 0.081 0.069 0.071 0.069 0.071 0.069 0.083 0.119 0.128	0.14 0.004 0.199 0.038 0.092 0.103 0.004 0.037 0.042 0.0124 0.02 0.0164 0.043 0.115 0.051 0.116 0.057 0.006 0.006
1.35	0.43	0.064	0.175



## APPENDIX C

DERIVATION OF EXPRESSIONS FOR CALCULATING  $P_{H_2S}$  AND  $P_{CO_2}$  USING THE MODEL OF KLYAMER ET AL.



### Using the Model of Klyamer Et Al.

$$P_{H_2S} = \frac{[H_2S]}{H_{H_2S}}$$

From equation 7,  $[H_2S] = \frac{\gamma^2[HS^-][H^+]}{K_{1C}}$ 

Therefore,

$$P_{H_2S} = \frac{\gamma^2 [HS^-] [H^+]}{K_{1C} H_{2S}}$$

Neglecting  $[S^{2-}]^{11,12}$ , from equation 3

$$[HS^{-}] = MX_{H_{2}S} - [H_{2}S] = MX_{H_{2}S} - P_{H_{2}S} H_{H_{2}S} = A$$

$$P_{H_2S} = \frac{\gamma^2 A[H^+]}{K_{1C} H_{2S}}$$

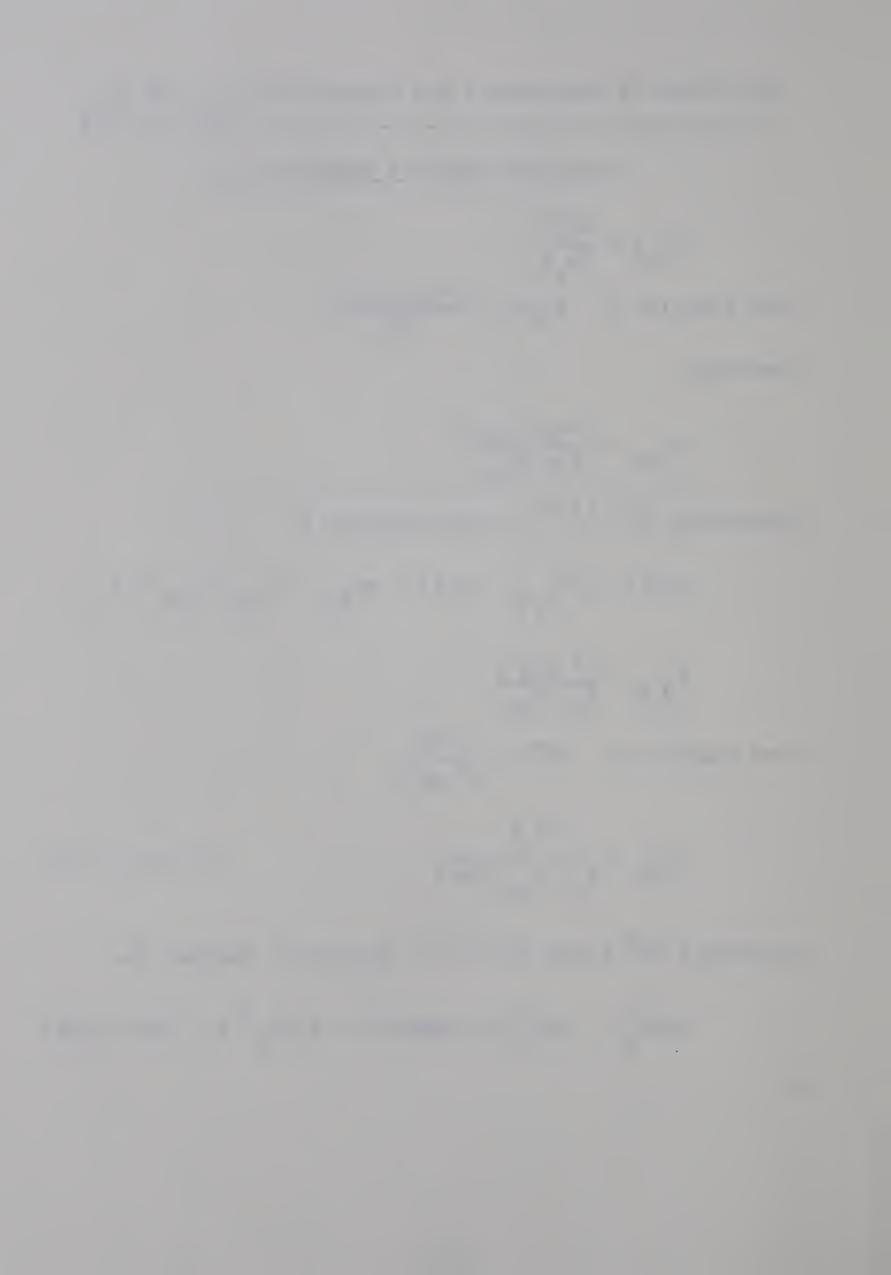
From equation 6, [H<sup>+</sup>] =  $\frac{\alpha K_{W}}{\gamma^{2} [OH^{-}]}$ 

$$P_{H_2S} = \frac{\alpha K_w^A}{K_{1C} H_{H_2S}[OH^-]} ------ (I)$$

Neglecting  $[S^{2-}]$  and  $[H^{+}]^{11,12}$ , equation 1 reduces to:

$$[RNH_3^+] = [HCO_3^-] + [RNHCOO] + 2[CO_3^{2-}] + [OH_] + [HS_]$$

or



$$[RNH_3^+] = mX_{CO_2} - P_{CO_2} H_{CO_2} + A + [CO_3^{2-}] + [OH^-]$$

$$= B + A + [CO_3^{2-}] + [OH^-] ------(i)$$

substituting  $[RNH_3^+]$  from equation 5 into equation (i)

$$\frac{K_{i}\alpha\alpha^{2}[RNH_{2}]}{\gamma^{2}[OH^{-}]} = A + B + [CO_{3}^{2-}] + [OH^{-}] \qquad ----- (ii)$$

substituting for  $[RNH_2]$  from equation 4 and simplifying for  $[RNH_3^+]$ ,

$$[RNH_{3}^{+}] = \frac{K_{i} \alpha \alpha^{2} (m-z)}{\{\gamma^{2} [OH^{-}] + K_{i} \alpha \alpha^{2}\}} = (A + B) + [CO_{3}^{2}] + [OH^{-}]$$

 $[{\rm CO}_3^{2-}]$  and  $[{\rm OH}^-]$  are considered when  ${\rm X}_{{\rm CO}_2}$  is less than 0.01 moles/mole of EA.

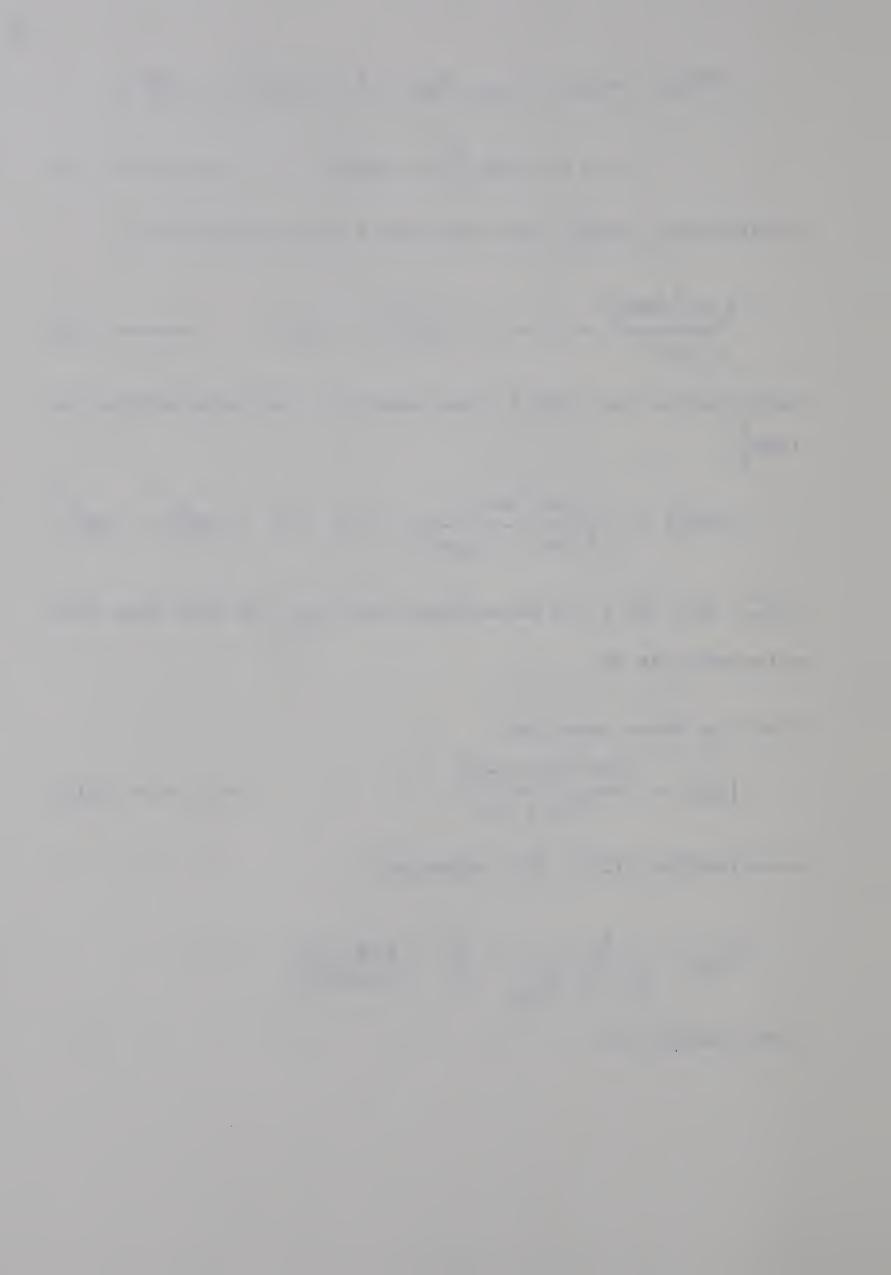
From the above equation;

$$[OH^{-}] = \frac{K_{i} \alpha \alpha^{2} (m-z-A-B)}{\gamma^{2} (A + B)}$$
 ----- (iii)

substituting (iii), into equation I.

$${}^{P}_{H_{2}S} = \frac{{}^{K}_{W}}{{}^{K}_{1C} {}^{K}_{1} {}^{H}_{H_{2}S}} \cdot \frac{\gamma^{2}}{\alpha \alpha} \cdot \frac{A(A + B)}{(m-z-A-B)}$$

From equation 10,



$$P_{CO_{2}} = \frac{1}{K_{m}} \cdot \frac{\gamma^{2}}{\alpha^{2}\alpha^{2}} \cdot z \cdot \frac{[RNH_{3}^{+}]}{[RNH_{2}]^{2}}$$

$$= \frac{1}{K_{m}} \cdot \frac{\gamma^{2}}{\alpha^{2}\alpha^{2}} \cdot z \cdot \frac{K_{i} \alpha \alpha^{2}}{\gamma^{2}[OH^{-}][RNH_{2}]}$$
-------(II)

From equation 4,

$$[RNH_2] = m - z - [RNH_3^+] = m-z-A-B$$
 ----- (iv)

substituting (iii) and (iv) in (II):

$$P_{CO_2} = \frac{1}{K_m} \cdot \frac{\gamma^2}{\frac{2}{a^2}} \cdot \frac{z(A + B)}{(m-z-A-B)^2} \qquad ----- (15)$$

From equation 2,

$$[RNHCOO] = z = mX_{CO_2} - P_{CO_2} H_{CO_2} - [HCO_3] - [CO_3^{2-}]$$

$$= B - [HCO_3]$$

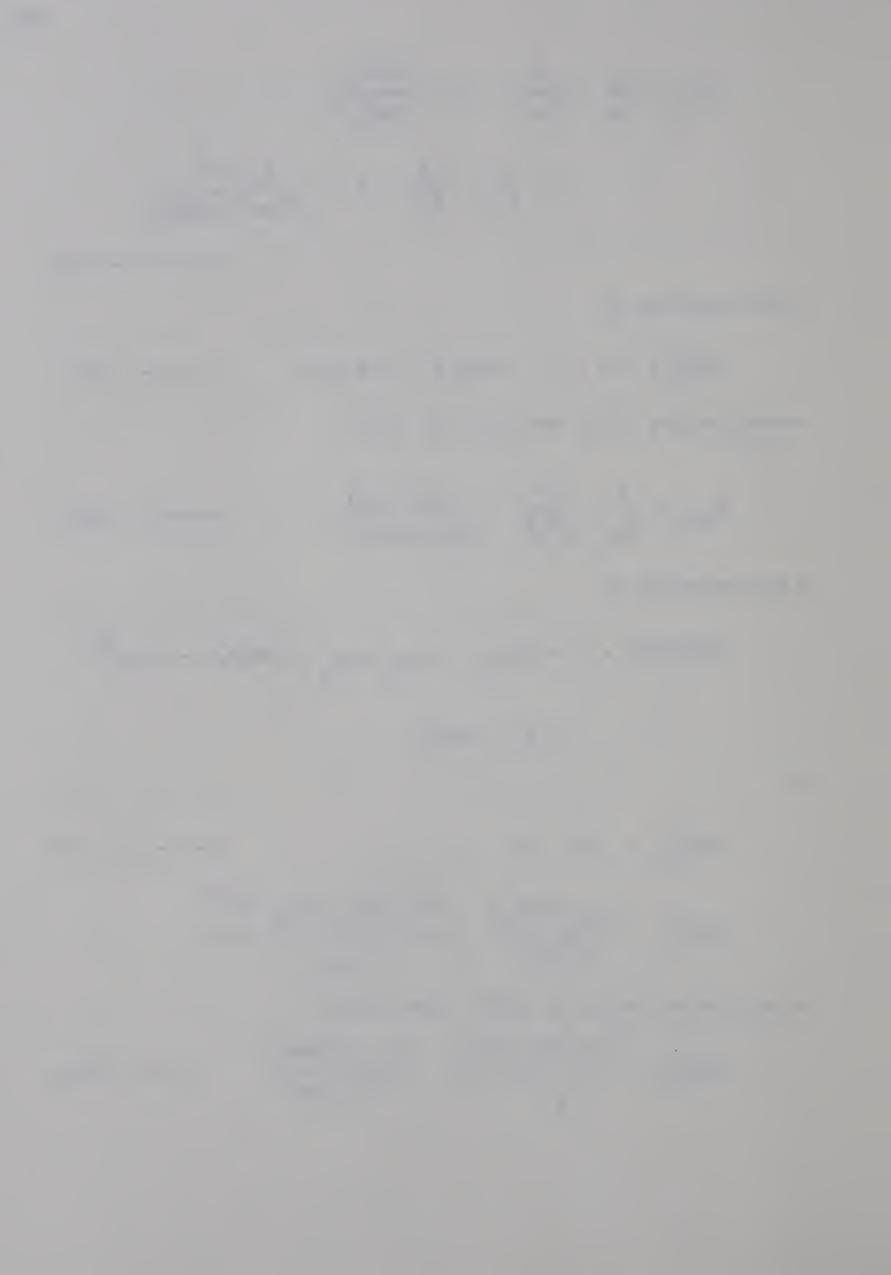
or

$$[HCO_{3}^{-}] = (B - z) \qquad ----- (v)$$

$$[HCO_{3}^{-}] = \frac{K_{1Y} \alpha [CO_{2}]}{\gamma^{2} [H^{+}]} = \frac{K_{1Y} H_{CO_{2}} P_{CO_{2}}}{K_{-}}$$

substituting value of [OH ] from (iii)

$$[HCO_{3}^{-}] = \frac{K_{1Y} H_{CO_{2}} P_{CO_{2}}}{K_{w}} \cdot \frac{K_{i} \alpha \alpha^{2} [RNH_{2}]}{\gamma^{2} (A+B)} ----- (vi)$$



From equation 10,

$$\frac{1}{K_{\rm m}} = \frac{\alpha^2 \alpha^2 \left[ \text{RNH}_2 \right]^2 P_{\text{CO}_2}}{\gamma^2 \left[ \text{RNH}_3^+ \right] \left[ \text{RNHCoo} \right]}$$

Multiplying equation (vi) by  $\frac{a [RNH_2]}{a [RNH_2]} \cdot \frac{[RNHCOO]}{[RNHCOO]}$  ( = 1 )

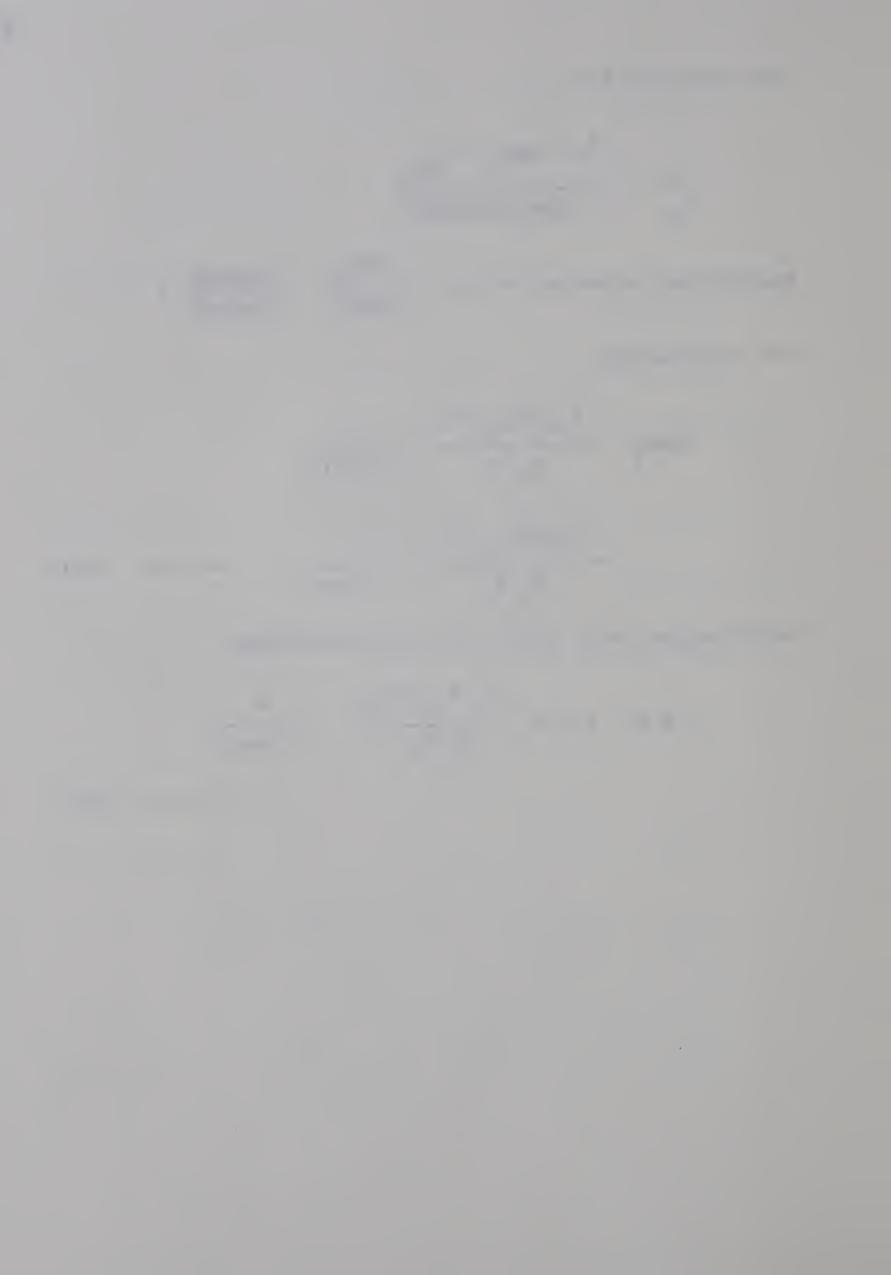
and rearranging,

$$[RNH_{2}] = \frac{K_{1Y} + CO_{2} + K_{i}}{K_{w} + K_{m}} \cdot \frac{z}{\alpha + [HCO_{3}^{-}]}$$

$$= \frac{K_{1Y} + CO_{2} + K_{i}}{K_{w} + K_{m}} \cdot \frac{z}{\alpha + (B-z)} ------ (vii)$$

substituting (vii) into (iv) and rearranging,

$$A = m - z - B - \frac{K_{i} K_{1Y} H_{CO_{2}}}{K_{w} K_{m}} \cdot \frac{z}{\alpha (B-z)}$$
----- (16)



#### APPENDIX D

PROOF THAT CHEMICAL EQUATIONS POSTULATED

IN THE TWO THEORETICAL MODELS ARE EQUIV
ALENT.



# PROOF THAT CHEMICAL EQUATIONS POSTULATED IN THE TWO THEORETICAL MODELS ARE EQUIVALENT

Zeggeren and Storey<sup>32</sup> have shown that the number of independent reactions possible for a given system is given by:

number of independent reactions

= number of species - rank of atom matrix.

For the system  $CO_2$ -H<sub>2</sub>S-water-EA,

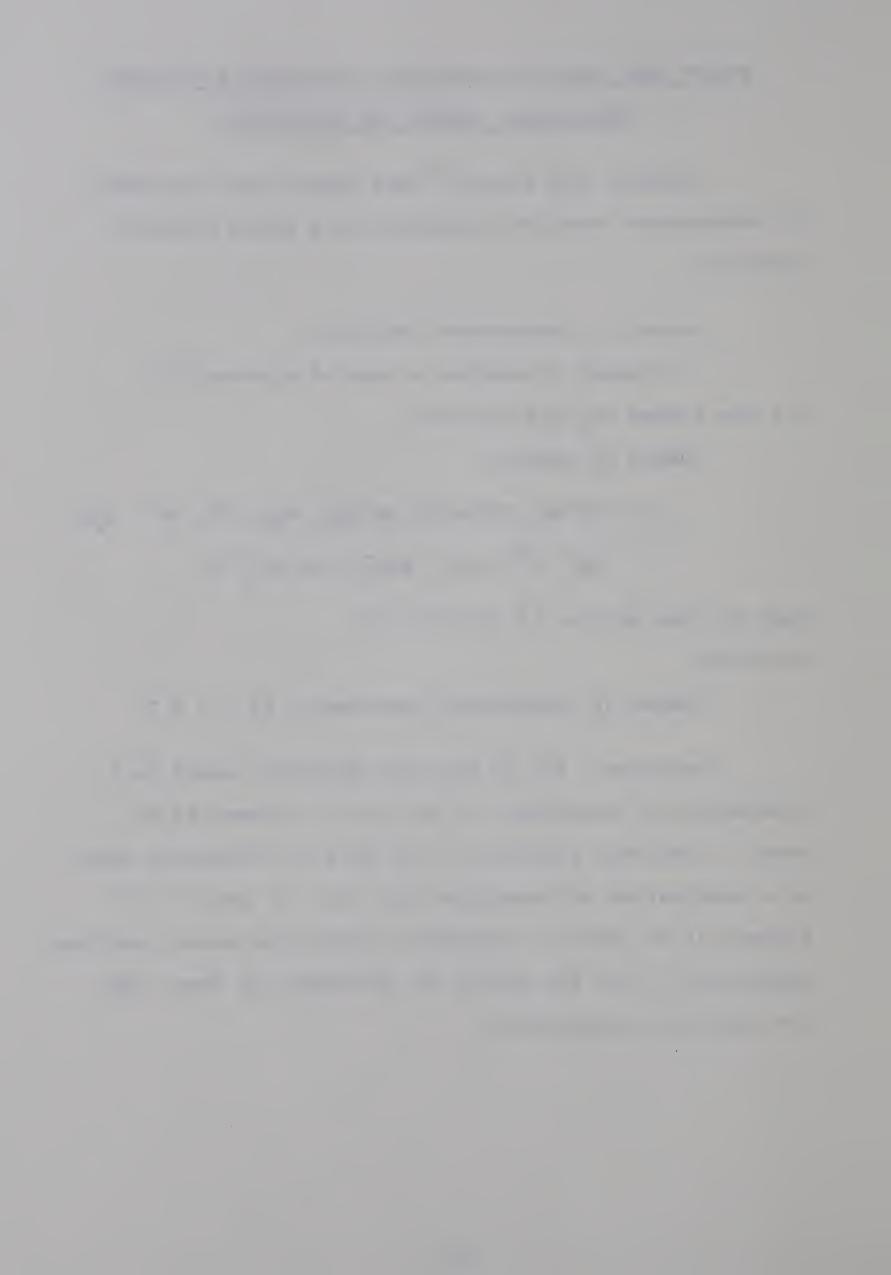
number of species

= 12 (RR'NH, RR'NCOŌ, RR'NH $_2^+$ , H $_2$ O, H $_2^+$ , OH $_3^-$ , HS $_3^-$ , CO $_2$ , HCO $_3^-$ , and CO $_3^{2-}$ ).

Rank of atom matrix = 5 (N,C,H,O,S).
Therefore,

number of independent reactions = 12 - 5 = 7

Reaction - (1) of Kent and Eisenberg model is a combination of reactions (a) and (c) of Klyamer et al. model. Similarly reaction (2) of Kent and Eisenberg model is a combination of reactions (a), (c), (e) and (f) of Klyamer et al. model. Therefore, though the seven reactions postulated in the two models are different in form, they are chemically equivalent.



### APPENDIX E

# COMPARISONS OF PREDICTED PARTIAL PRESSURES WITH EXPERIMENTAL DATA

Experimental Data*
Prediction by Klyamer et al. model
• Prediction by Kent and Eisenberg model
Prediction by Modified Klyamer et al. model
* of Lee, Otto and Mather for figures 9 to 24;
of this work for figures 25 and 26.



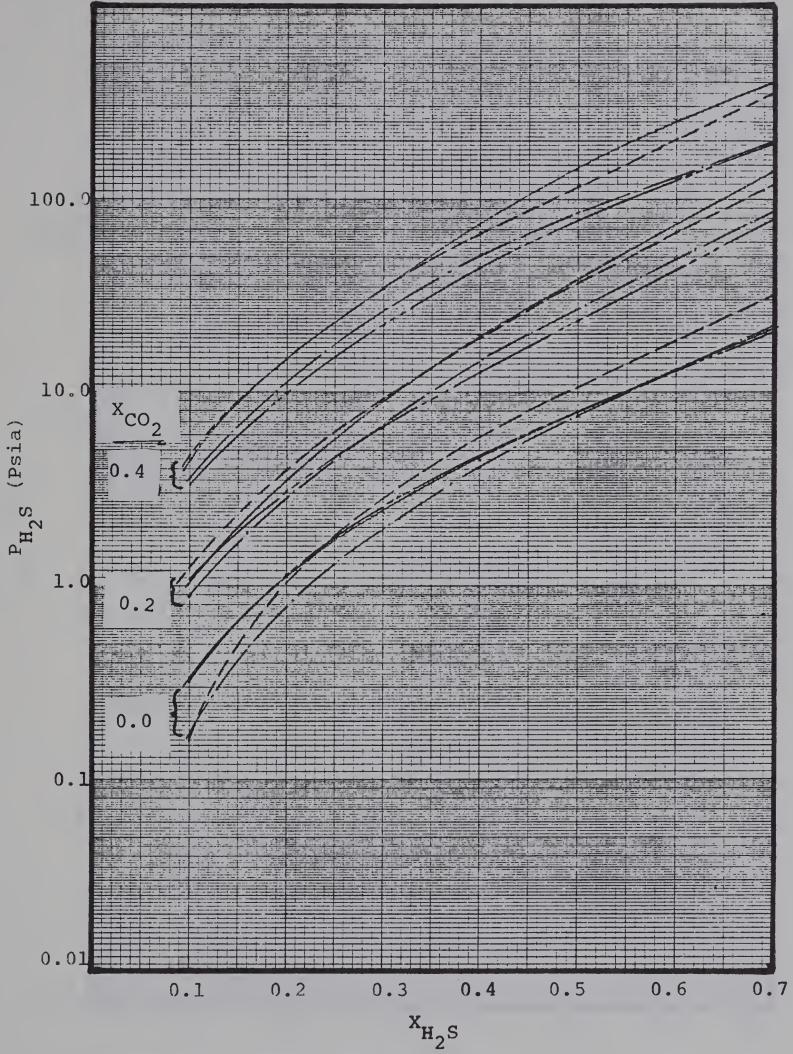


Figure 9 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 2.5 N MEA at 100°C, with Published Data.



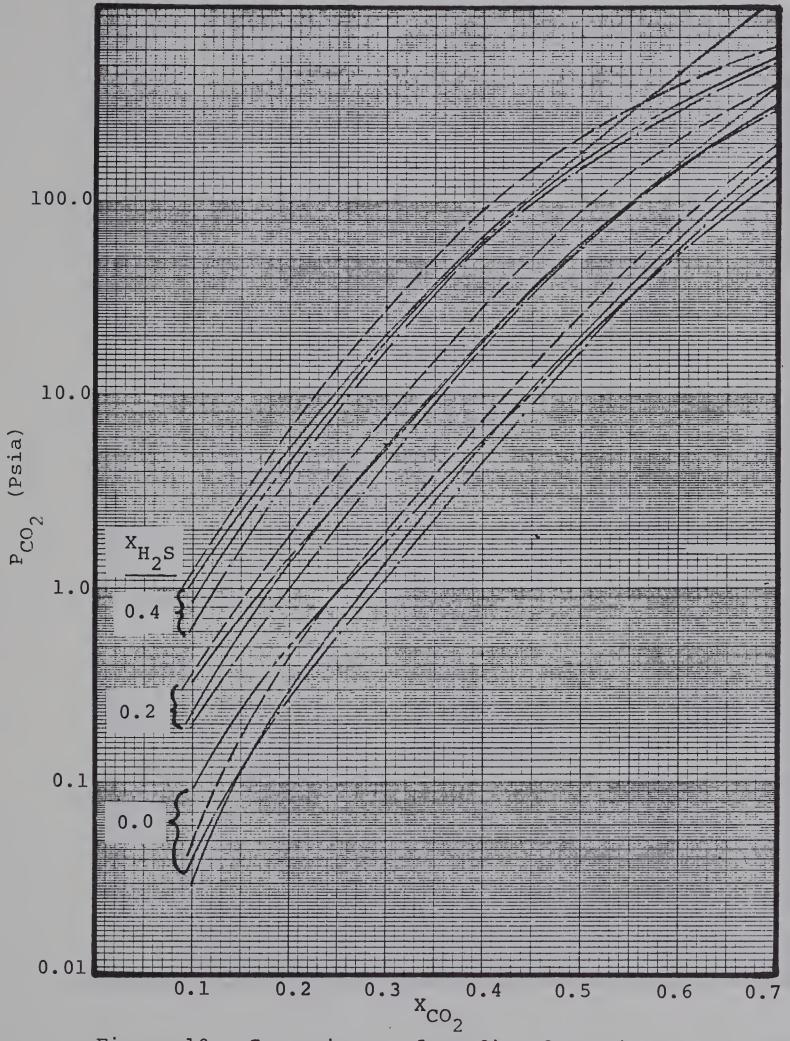


Figure 10 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 2.5 N MEA at 100°C, with Published Data.



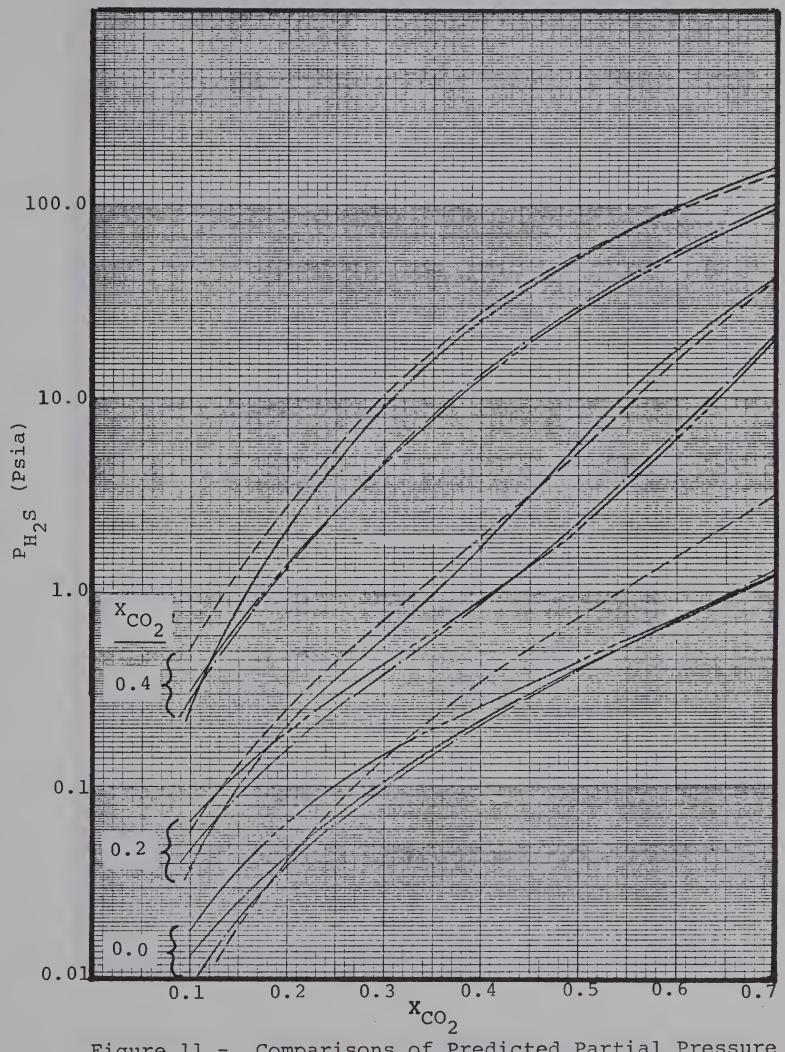
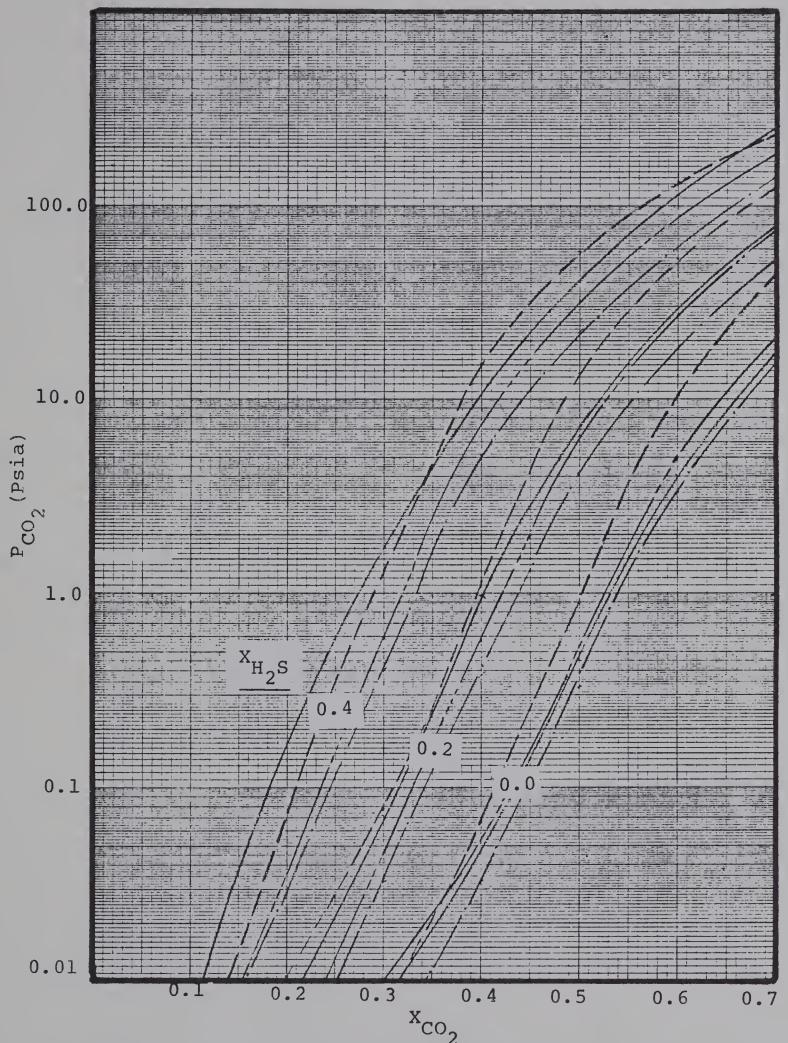


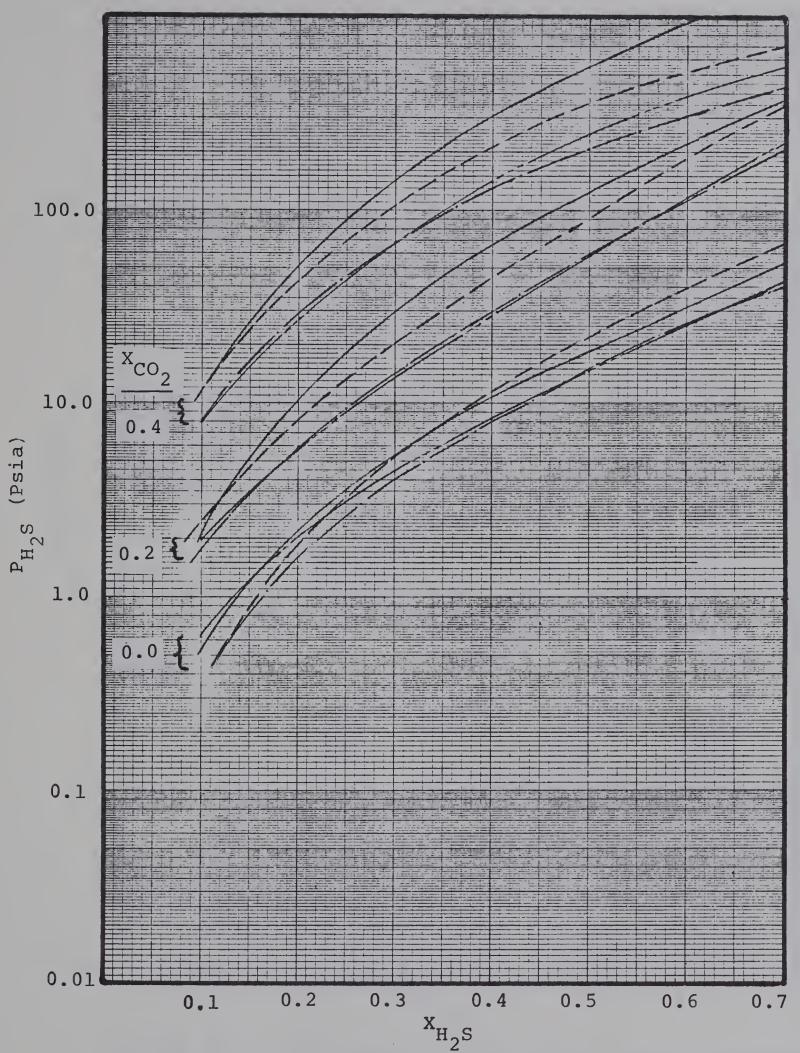
Figure 11 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 2.5 N MEA at 40°C, with Published Data.





X<sub>CO<sub>2</sub></sub>
Figure 12 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 2.5 N MEA at 40°C, with Published Data.





XH<sub>2</sub>S
Figure 13 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 5 N MEA at 100°C, with Published Data.



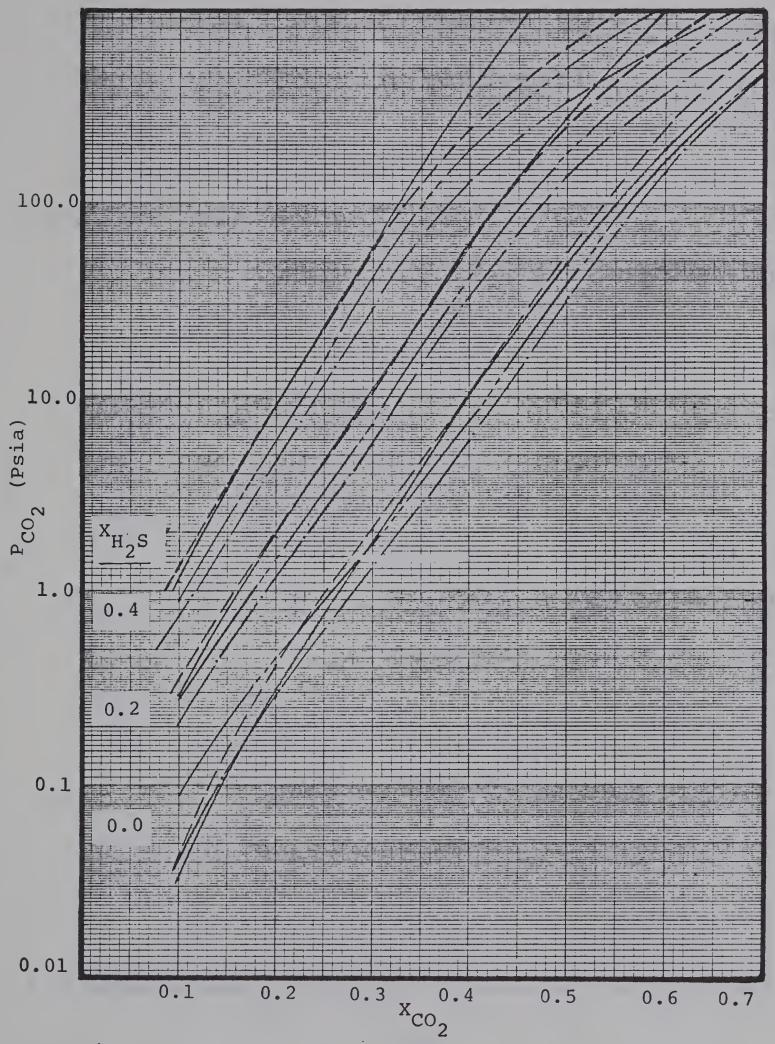


Figure 14 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 5 N MEA at 100°C, with Published Data.



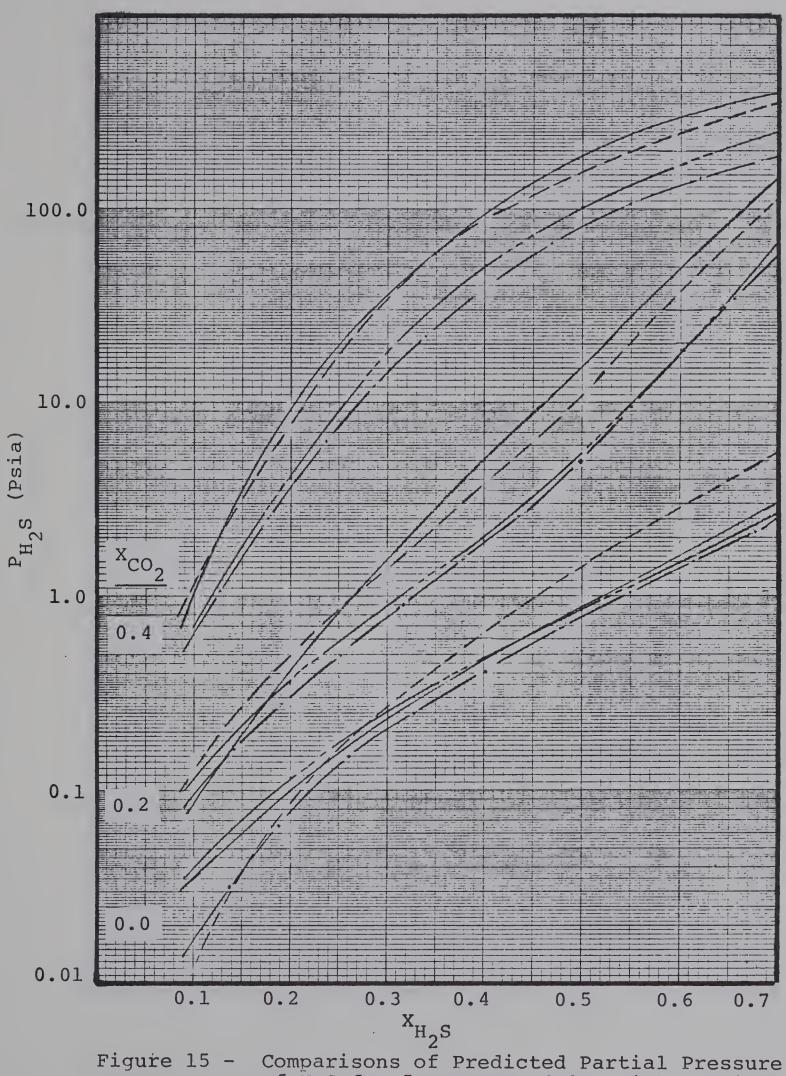


Figure 15 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 5 N MEA at 40°C, with Published Data.



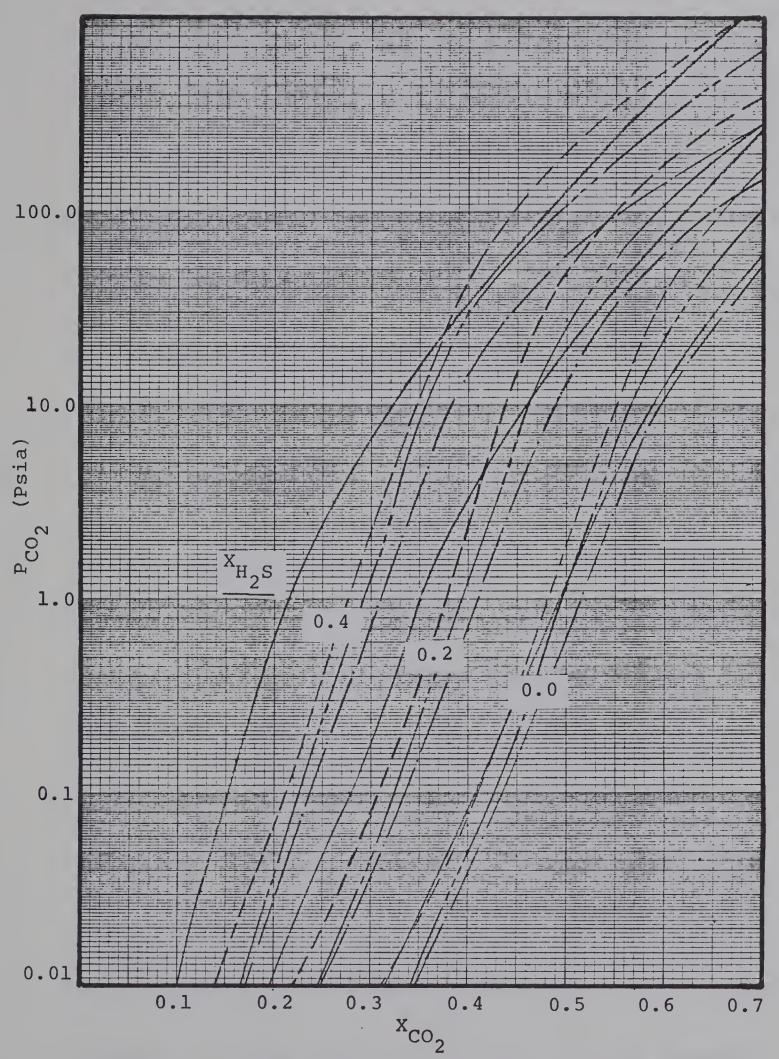


Figure 16 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 5 N MEA at 40°C, with Published Data.



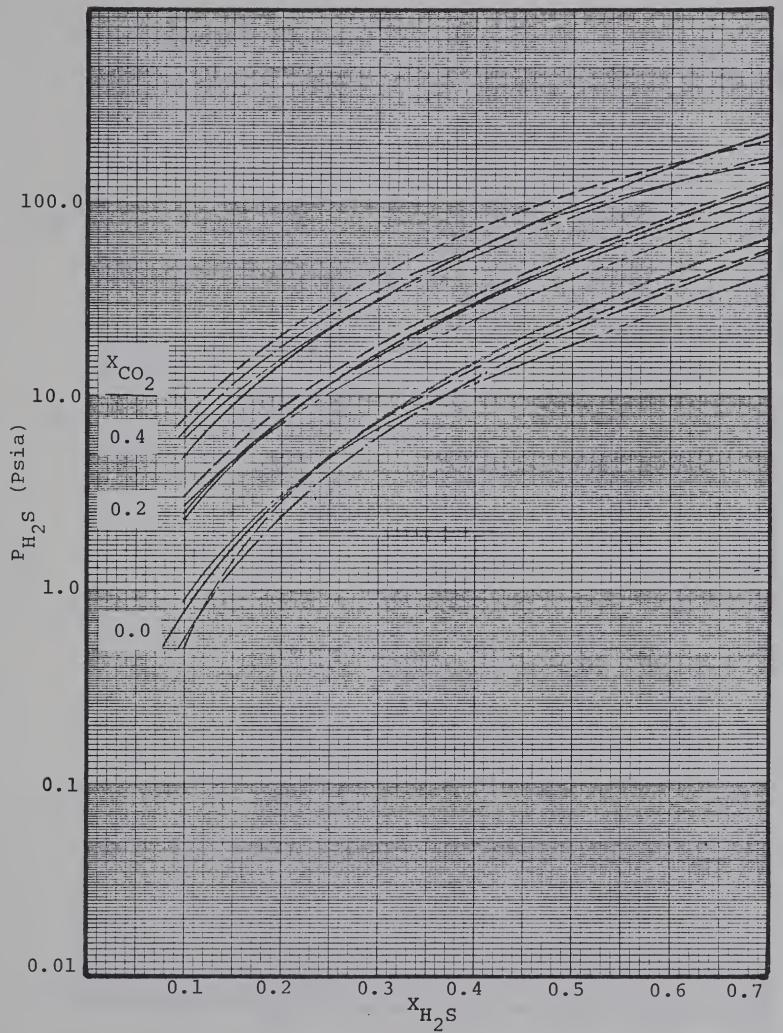


Figure 17 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 2 N DEA at 100°C, with Published Data.



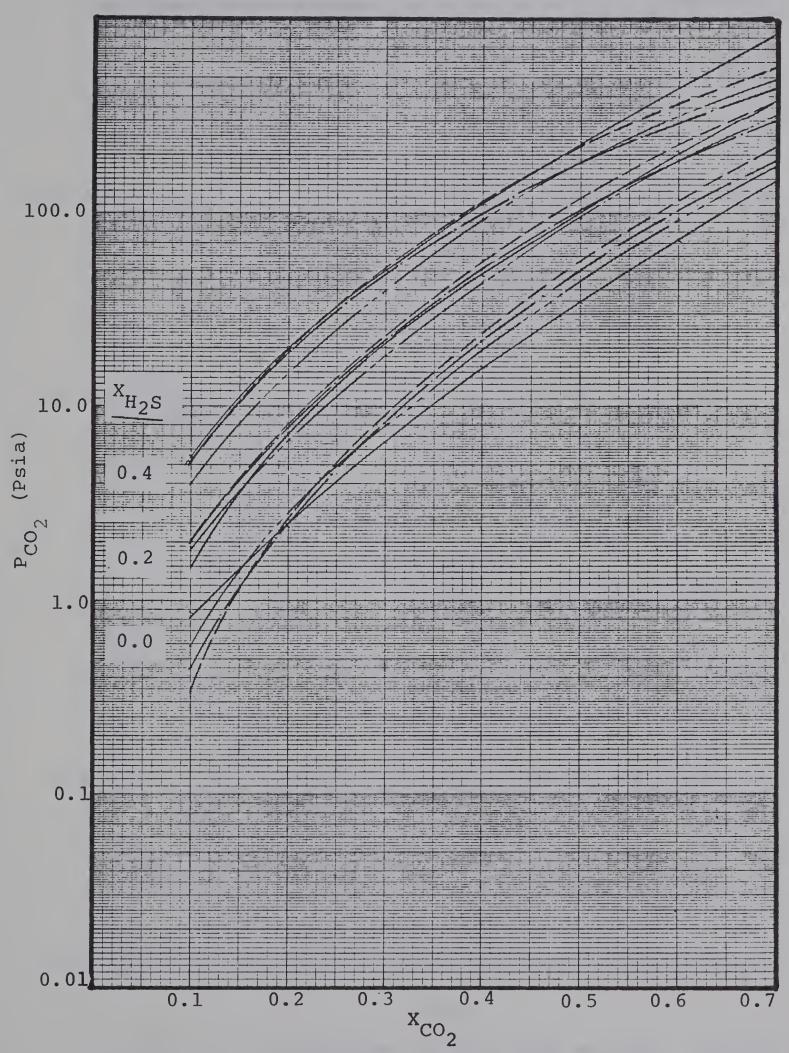


Figure 18 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 2 N DEA at 100°C, with Published Data.



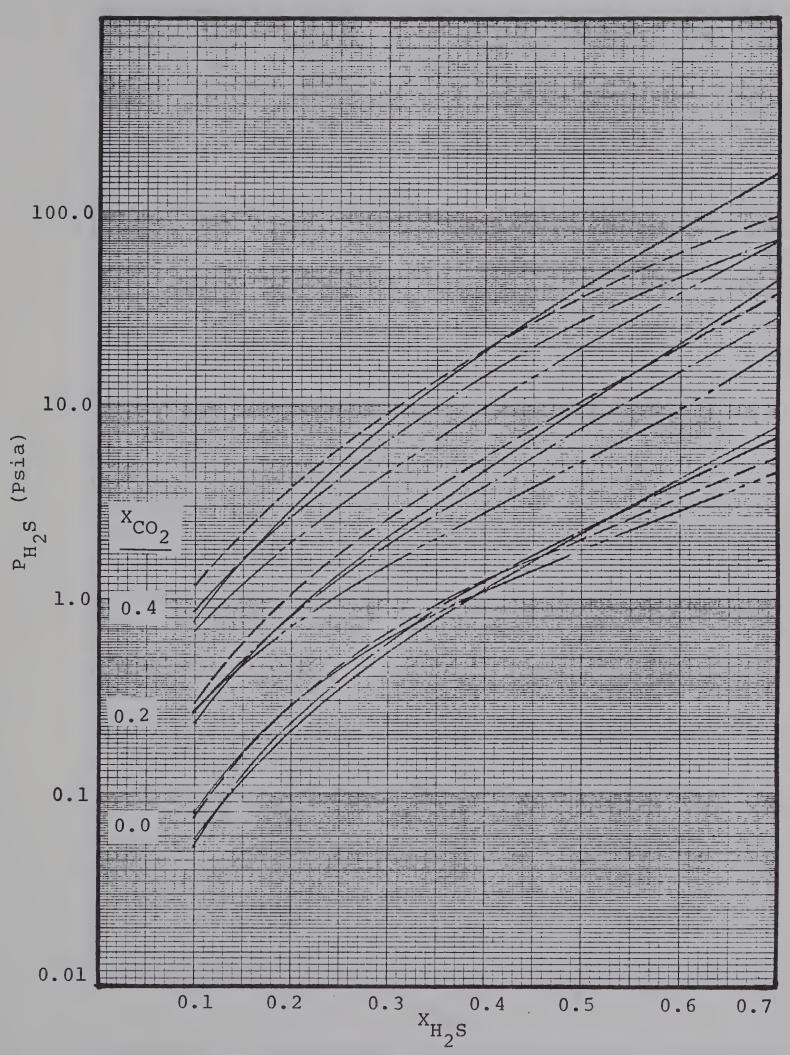


Figure 19 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 2 N DEA at 50°C, with Published Data.



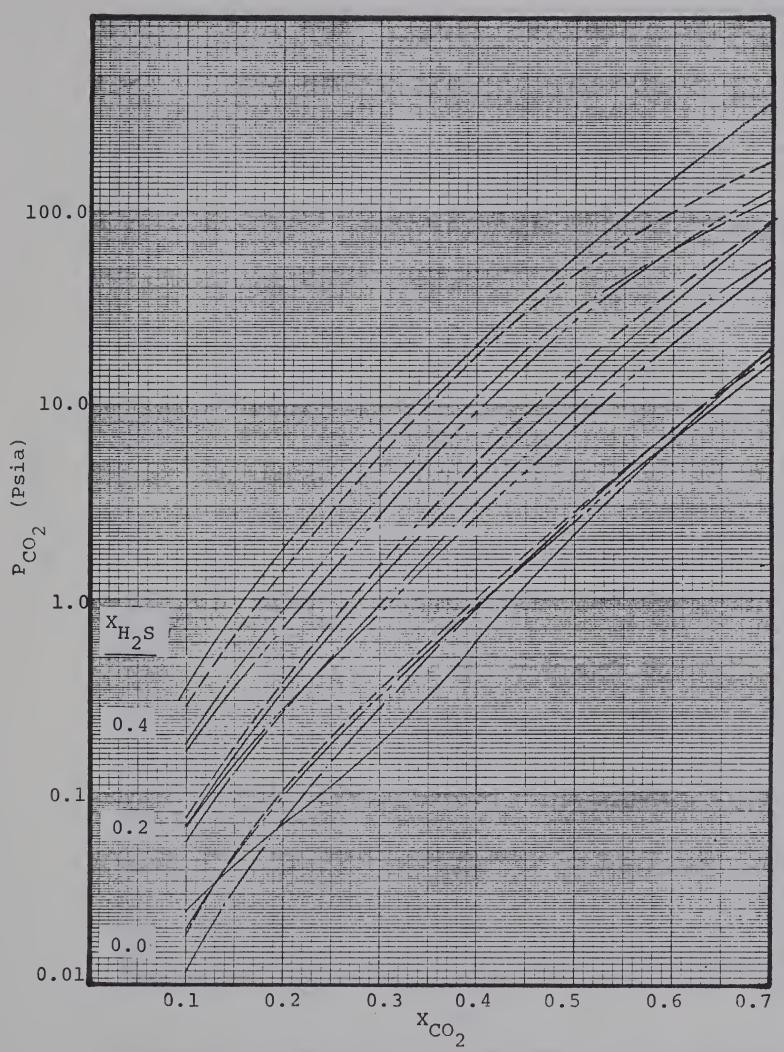


Figure 20 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 2 N DEA at 50°C, with Published Data.



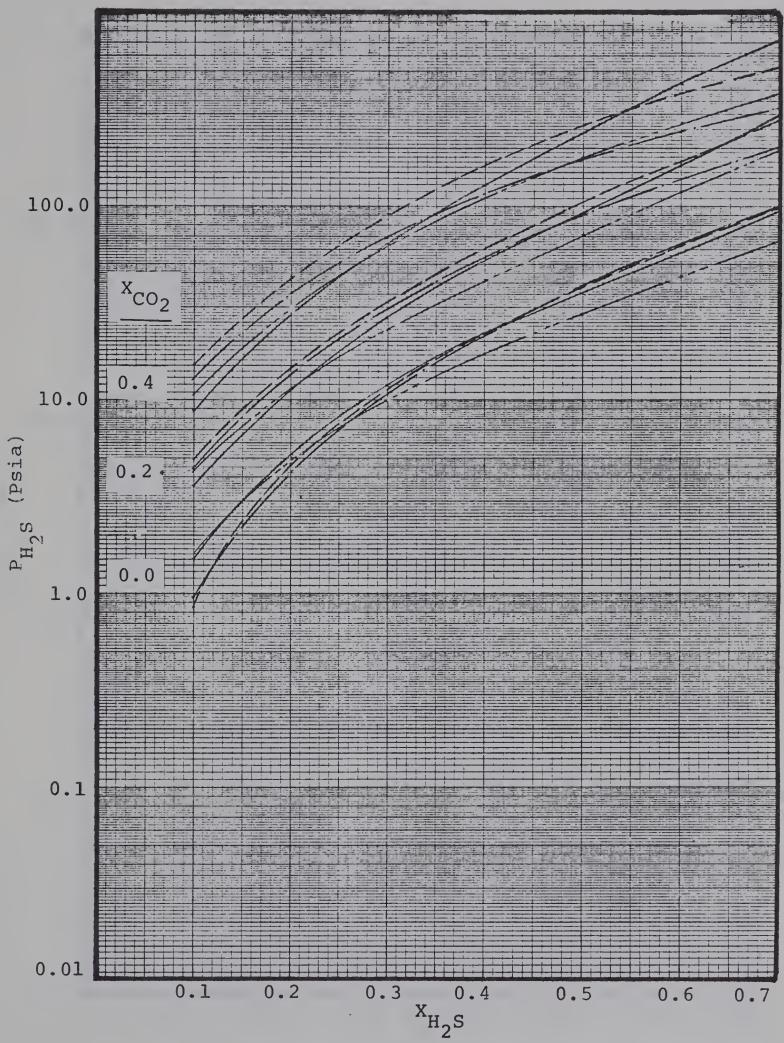


Figure 21 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 3.5 N DEA at 100°C, with Published Data.



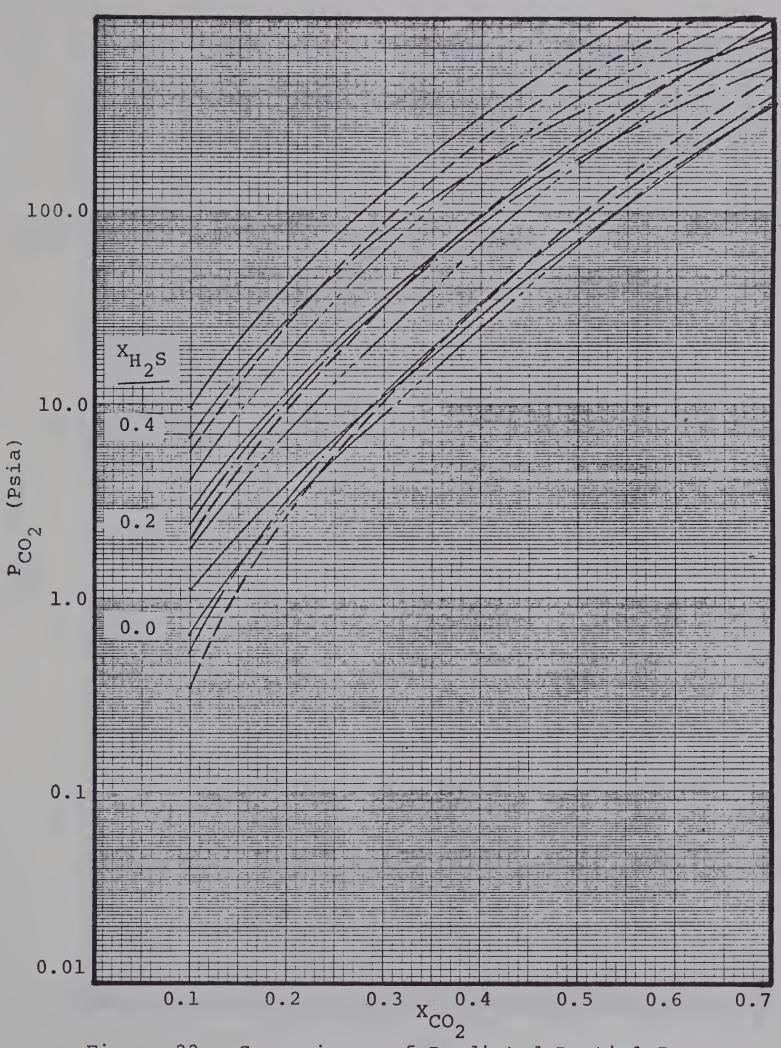


Figure 22 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 3.5 N DEA at 100°C, with Published Data.



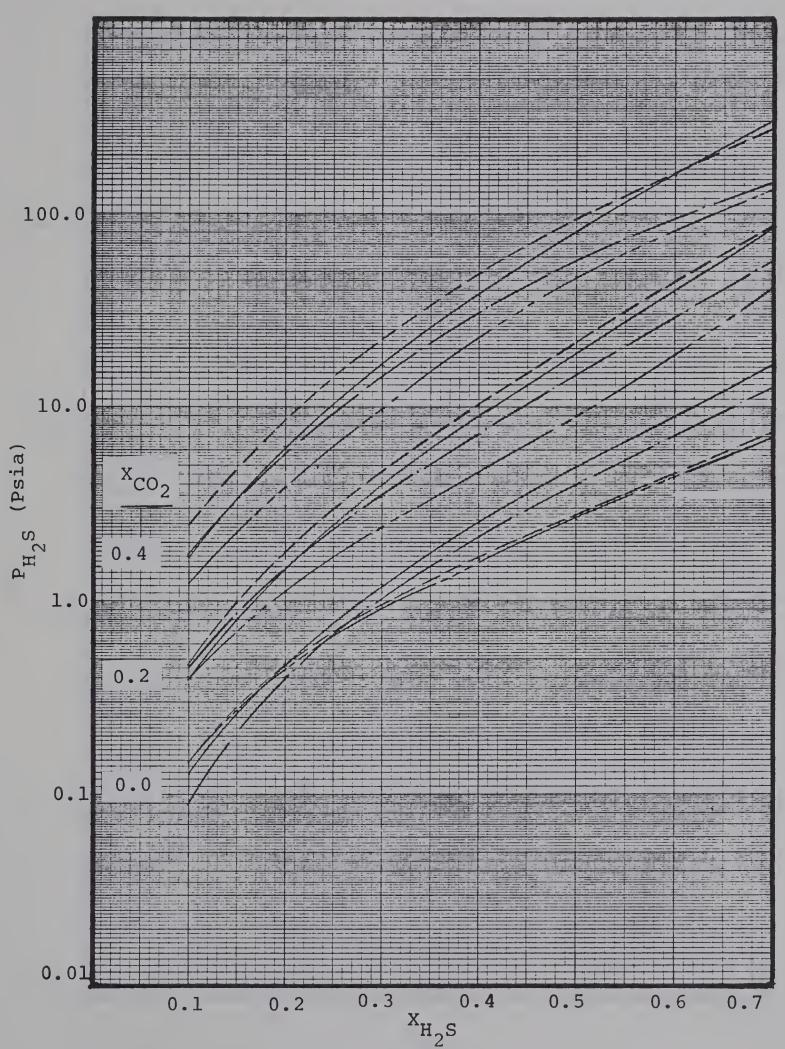
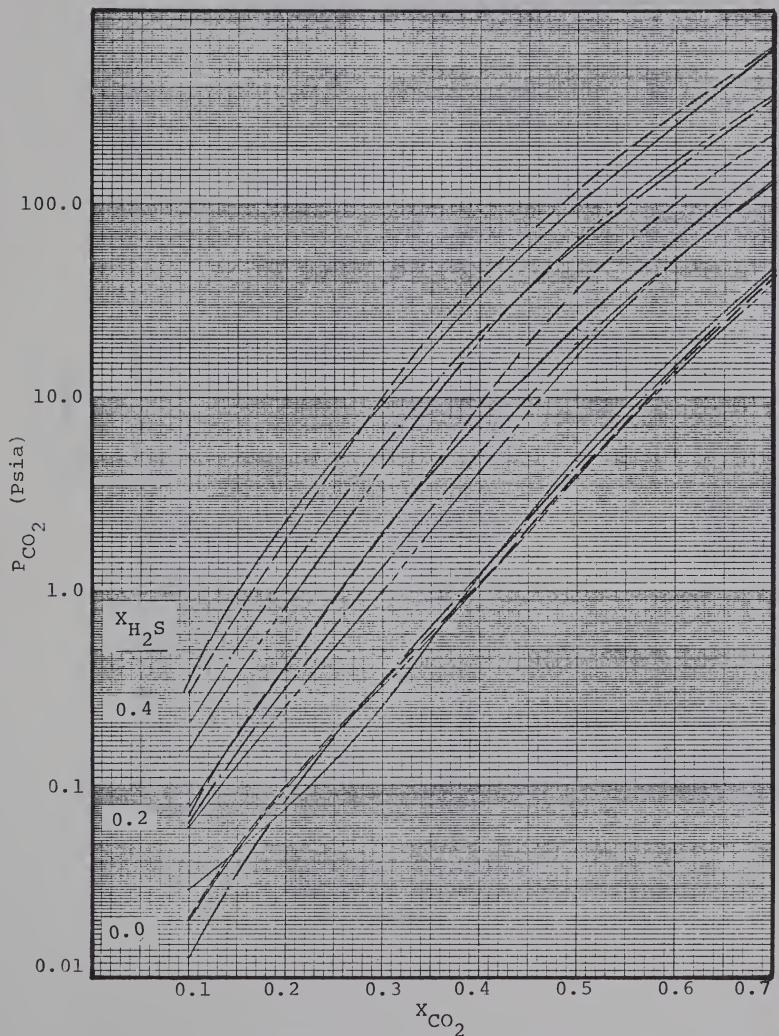


Figure 23 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 3.5 N DEA at 50°C, with Published Data.





XCO<sub>2</sub>
Figure 24 - Comparisons of Predicted Partial Pressures of CO<sub>2</sub> for 3.5 N DEA at 50°C, with

Published Data.



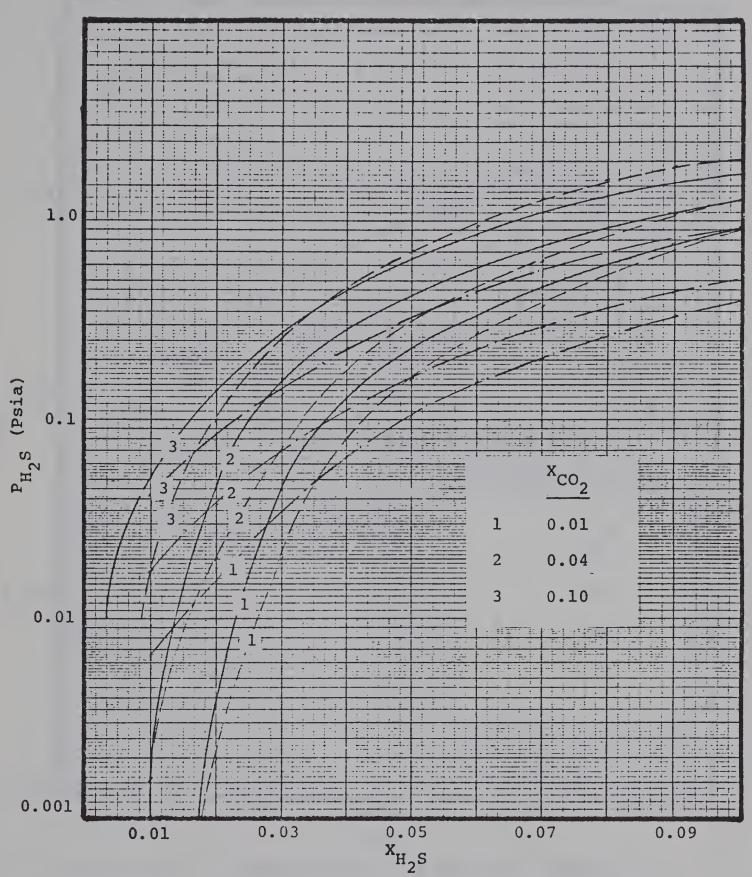


Figure 25 - Comparisons of Predicted Partial Pressure of H<sub>2</sub>S for 5 N MEA at 100°C, with Data Obtained in This Study.



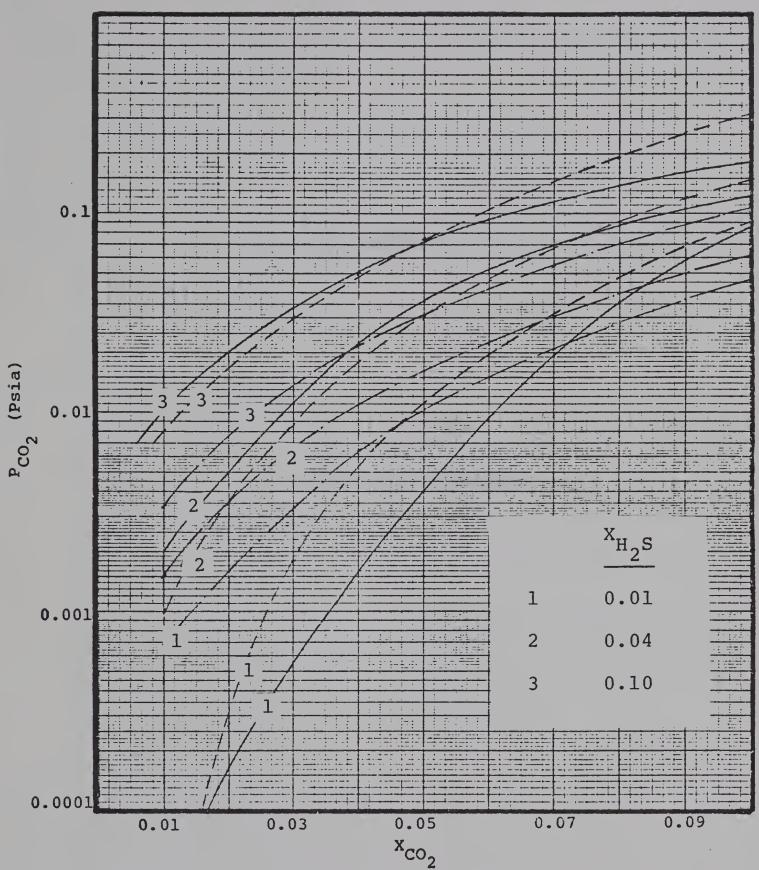


Figure 26 - Comparisons of Predicted Partial Pressure of CO<sub>2</sub> for 5 N MEA at 100°C, with Data Obtained in This Study.



APPENDIX F

COMPUTER PROGRAMS



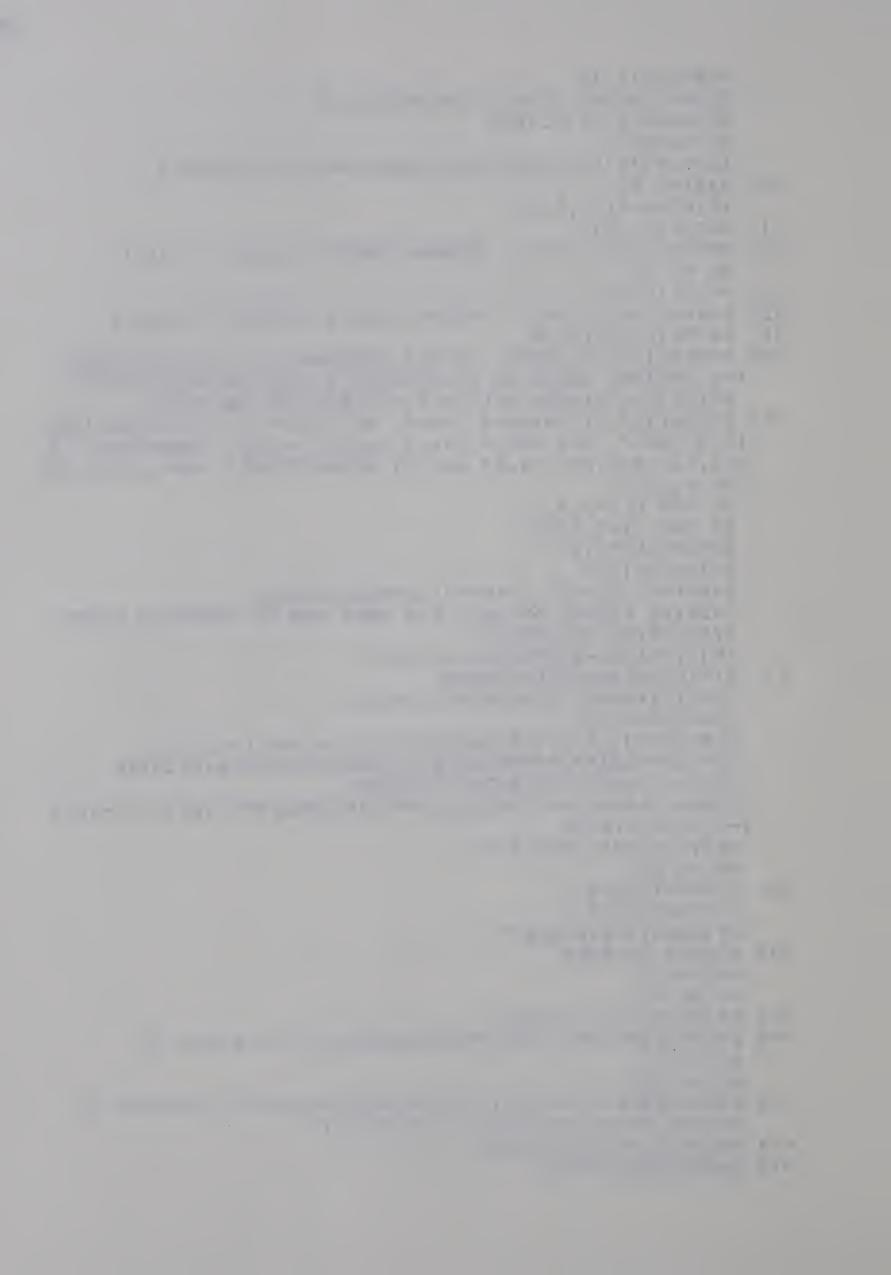
```
PROGRAM FOR CALCULATION OF PARTIAL PRESSURES OF H2S AND *
 *
   CO2 OVER ETHANOLAMINE SOLUTIONS ----
                                        USING MODIFIED
   KLYAMER ET AL. MODEL
 *
    INPUT VARIABLES FOR THE PROGRAM ARE
 *
    T - TEMPERATURE IN DEGREE KELVIN
 *
     MM - MOLES OF ETHANOLAMINE PER 1000.0 GRANS OF WATER
 *
    KLMN = 1 FOR MONO- AND 2 FOR DI-ETHANOLAMINE
 *************************
     REAL KIY, KI, KW, KIC, K2C, MA1, MA2, K1, KM, MU, MM, K2Y
     DIMENSION DD (3)
     DIMENSION Y (3), PHI (3)
     DO 101 I=1,3
     PHI(I) = 0.0
 101 CONTINUE
     READ (5, 1) T, MM, KLMN
1
     FORMAT (2F15.5, I1)
C
     DETERMINATION OF VARIOUS PARAMETERS FOR THE ABOVE READ COND
     TT=1000.0/T
     YY=0.872446E01-0.183312E01*TT+0.33752E00*TT**2
     KIY=EXP(-2.303*YY)
     YH=-0.450823E01+0.453045E-01*T-0.580136E-04*T**2
     HH2S=EXP(-2.303*YH)
     YC=-0.248352E01+0.361175E-01*T-0.440596E-04*T**2
     HCO2 = EXP(-2.303 * YC)
     TW = (T-273.16) *1.8+32.0
     YW=-0.756413+0.278931E-01*TW-0.700393E-04*TW**2+0.747623E-0
     KW = EXP(2.303*(YW-15.0))
     YIC=0.110835+0.166718E-01*TW-0.684879E-04*TW**2+0.106972E-0
     KIC = EXP(2.303 * (YIC - 8.0))
     E2=-0.290239E04/T+7.0880-0.2379E-01*T
     K2Y = EXP(2.303 * E2)
     K2C=0.1E-15
     IF(KLMN-2)2,3,3
 2
     IF (0.10E04/T-2.95)4,7,7
     MA2=0.47424E04*(1.0/T-0.0025)-3.6341
     KM = EXP(MA2 * 2.303)
     GO TO 10
 7
     MA1=0.458E04*(1.0/T-0.00295)-1.50
     KM = EXP(MA1 * 2.303)
 10
     YIM = -2677.91/T - 0.6169 - 0.4277E - 03*T
     E3 = EXP(2.303 * YIM)
     KI=KW/E3
     AA = 0.8727
     GO TO 20
 3
     DA=0.36585E04*(1.0/T-0.0026)-4.0
     KM = EXP(DA*2.303)
```



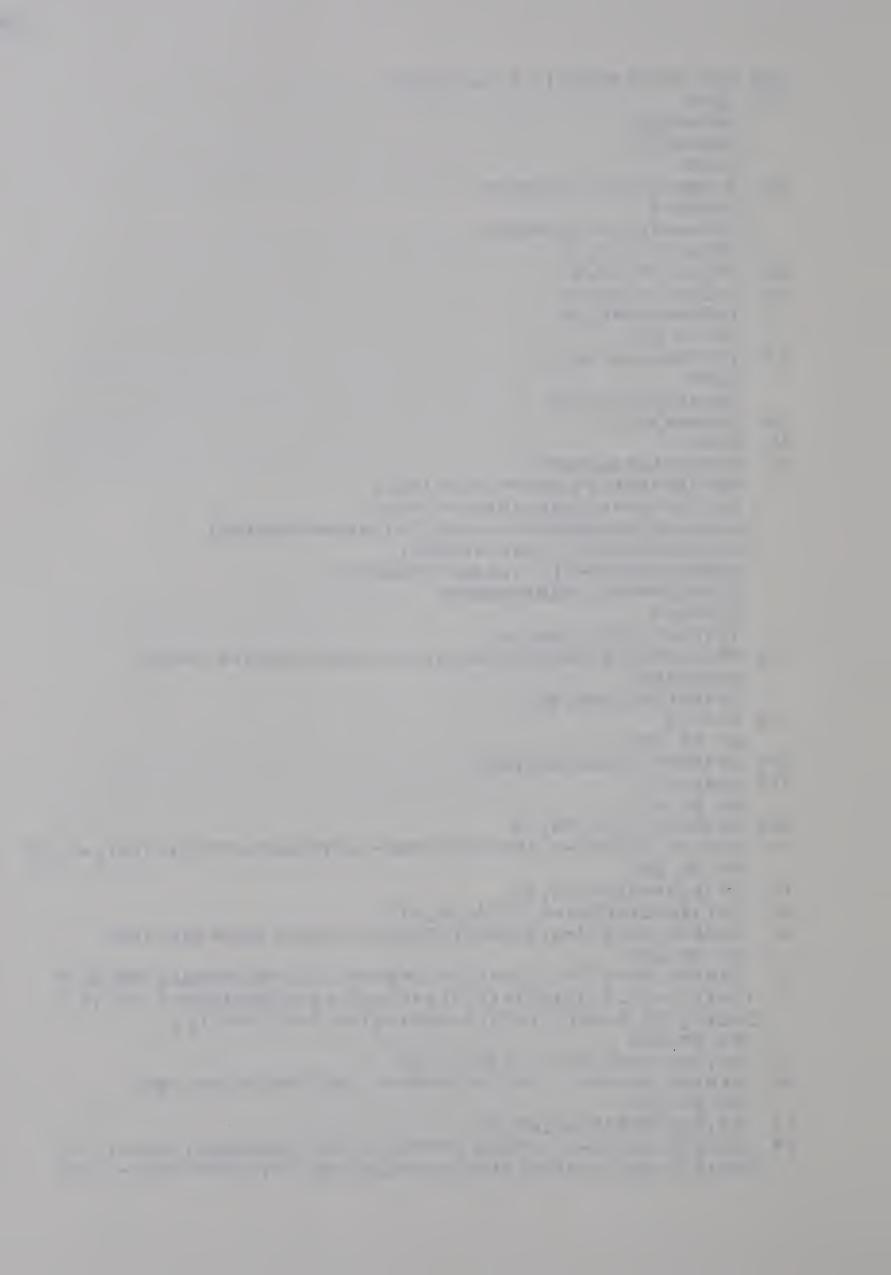
```
TTT = T - 273.16
    YID=-1.609+0.41486E-01*(TTT-37.8)
    E33=EXP(YID)/0.1E09
    KI = KW / E33
    AA=0.857478+0.125767D-01*MM+0.44202D-02*MM**2
20
    GAMA=0.50
    IF(KLMN-1)21,21,22
    WRITE (6, 221)
221 FORMAT (1H1,/,10X,' ETHANOL AMINE PRESENT IS MEA')
    GO TO 18
    WRITE (6,222)
222 FORMAT (1H1,/,10X,' ETHANOL AMINE PRESENT IS DEA')
    WRITE (6, 399) T, MM
399 FORMAT (//,2X,'TEMP. OF THE SYSTEM=',F7.2,//,2X,'CONC.
   10F ETHANOL AMINE IN MOLES/1000.0 GRAM OF H20=1,F5.2)
    WRITE (6,412) HH2S, HCO2, KIY, KIC, K2Y, K2C, KW, KM, KI
412 FORMAT (//, 2X, 'HENRYS CONST. FOR H2S=', E14.5, //, 2X, 'HEN
   1RYS CONST. FOR CO2=',E14.5,///,2X,'EQIL. CONSTANTS
   21Y, KIC, K2Y, K2C, KW, KM AND KI RESPECTIVELY ARE',//,2X,7E
   316.6,////
    DO 108 LLL=2,4,2
    DO 108 II=1,10,3
    XCO2=LLL/10.0
    XH2S=II/10.0
    ALPHA=55.51/(55.51+MM*(1.0+XCO2+XH2S))
    INITIAL VALUES OF PCO2 AND PH2S CAN BE OBTAINED USING
    SIMPLIFIED EQUATIONS
    IF (1.0-XH2S-2.0*XCO2) 68, 68, 67
67
    K1 = (KI*KIY*HCO2) / (KM*KW)
    CQ=K1/(AA*MM)+1.0-XH2S-2.0*XCO2
    QQ = XH2S + XCO2
    HCM = SORT((CO/2.0) **2 + (K1 * XCO2) / (AA * MM)) - CO/2.0
    QT = (KW*GAMA**2*MM*XH2S*QQ) / (KI*KIC*HH2S*AA*ALPHA)
    PH2S = QT / (HCM + 1.0 - XH2S - 2.0 * XCO2)
    PCO2= (GAMA**2*XCO2*QQ) / (KM* (AA*ALPHA) **2* (HCM+1.0-XH2S
   1-2.0*XCO2)**2)
    WRITE (6, 415) PCO2, PH2S
    GO TO 220
68
    A1=MM*XH2S*0.5
    B2=MM*XCO2*0.5
    IF (XH2S) 416,416,417
416 PCO2=2.0*B2/KM
    PH2S=0.0
    GO TO 418
417 IF (XCO2) 419, 419, 420
419 PH2S=(KW*A1**2)/(KIC*KI*HH2S*MM)*(1.0+XH2S/0.1)
    PCO2=0.0
    GO TO 418
420 \text{ PH2S} = (KW*A1*(A1+B2))/(KIC*KI*HH2S*MM)*(2.0+XH2S/0.1)
    PCO2=2.0*(A1+B2)/KM*(1.0+XCO2/0.1)
418 WRITE (6, 415) PCO2, PH2S
415 FORMAT (5X, E16.5)
```

C

C



```
220 \text{ Z} = 0.8 \times \text{MM} \times \text{XCO2} / (1.0 + 4.0 \times \text{XCO2})
231 ZZ = Z
     PHS=PH2S
     PCO=PCO2
    KL=0
40
    A1=MM*XH2S-HH2S*PH2S
    KL = KL + 1
    B2=MM*XCO2-HCO2*PCO2
    IF (A1) 81,82,82
82
    IF (B2) 81,83,83
81
     PH2S=0.95*PH2S
    PCO2=PCO2*0.95
    GO TO 231
83
    FFK=MM-Z-A1-B2
    KJ=0
    IF (FFK) 89,89,85
89
    FFK=MM/50.0
85
    HS=A1
12
    RN=KI*AA*ALPHA**2
    OH = (RN*FFK) / (GAMA**2*(A1+B2))
    HPLUS = (KW * ALPHA) / (GAMA * * 2 * OH)
    HCO3=(KIY*ALPHA*HCO2*PCO2)/(GAMA**2*HPLUS)
    CO3 = (K2Y*HCO3) / (GAMA*HPLUS)
    RNH3 = (RN*(MM-Z))/(GAMA**2*OH+RN)
    S2 = (K2C*HS) / (GAMA*HPLUS)
    KJ = KJ + 1
    IF (KJ-10) 106, 106, 303
106 MU=0.5*(Z+A1+HPLUS+OH+RNH3+4.0*CO3+HCO3+4.0*52)
    ETA=GAMA
    IF (MU) 300, 300, 301
300 MU = 2.0
    GO TO 302
301 IF (MU-7.0) 302, 302, 303
303 \text{ GAMA} = 0.5
    GO TO 93
302 IF (MU-0.1) 74,74,75
74
    GAMA=0.902308-0.199577E01*MU-0.678868E-01*(EXP(MU))+0.05
    GO TO 203
75
    IF(KLMN-2)54,55,55
54
    IF ((XCO2+XH2S)-0.2)56,56,57
    GAMA=0.399117-0.338402E-02*MU+0.324219E00*EXP(-MU)
56
    GO TO 203
57
    GAMA=0.399117-0.338402E-02*MU+0.324219E00*EXP(-MU)+0.1
   15* (1.0- (0.21/(XCO2+XH2S)) **0.95) + ((XCO2+XH2S-0.4)/(1.0
   2+EXP(-(7.2-MM)))*(1.1-EXP(-(374.0-T)/100.0))
    GO TO 203
55
    IF ((XCO2+XH2S)-0.2)58,58,59
58
    GAMA = 0.36640 - 0.15975E - 01 * MU + 0.344379E00 * EXP(-MU)
    GO TO 203
59
    IF (XCO2*XH2S) 60,61,60
    GAMA = 0.36640 - 0.15975E - 01*MU + 0.344379E00*EXP(-MU) + (0.10)
   10*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.1*((XCO2+XH2S-0.05)
```

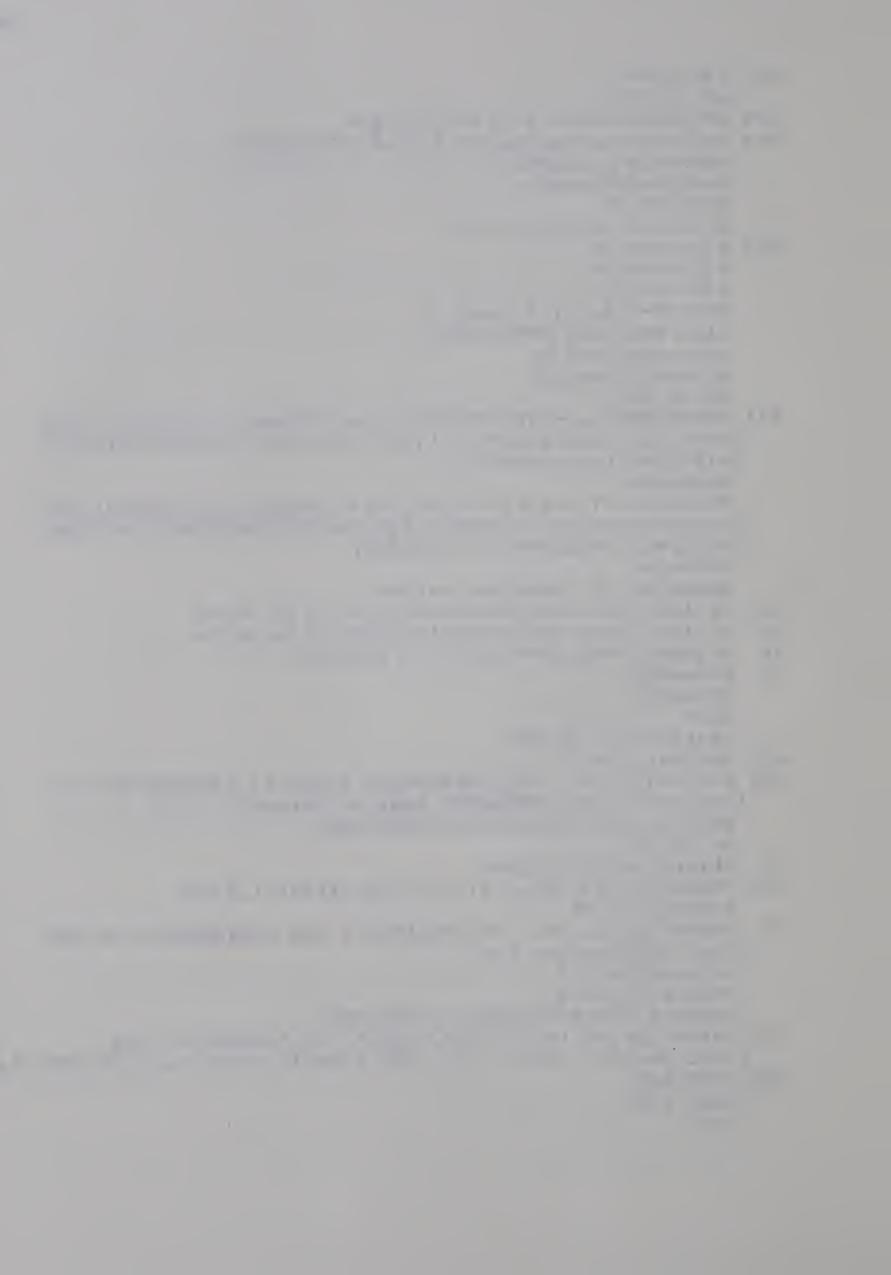


```
2/(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0)))*(1.05-EXP(
   3-(5.22-MM)/10.0)
    GO TO 203
   GAMA = 0.36640 - 0.15975E - 01 * MU + 0.344379E00 * EXP(-MU) + (0.10)
   1*(1.0-(0.21/(XCO2+XH2S))**0.90)+0.5*((XCO2+XH2S-0.30)/
   2(XH2S+XCO2))*(1.05-EXP(-(374.0-T)/100.0))
203 IF (ABS ((GAMA-ETA)/GAMA*100.0)-5.0) 93,93,12
    IF (XCO2) 91, 91, 92
    IF (XH2S) 94, 94, 204
92
91
    PKK= (KW*GAMA**2) / (KIC*KI*AA*ALPHA)
    PCC = SQRT ( ((1.0 - XH2S) / 2.0) **2 + PKK*XH2S)
    PH2S=MM/(HH2S*(1.0-PKK))*(PCC-(1.0-XH2S)/2.0-PKK*XH2S)
    PCO=0.0
    GO TO 933
94
    TK1 = (KI*KIY*HCO2*AA*ALPHA**2) / (KW*GAMA**2)
    TK2 = (KM*KW*AA) / (KI*KIY*HCO2)
    B2=MM*XCO2-PCO2*HCO2
    BB = (B2 - MM/2.0 - 0.50/TK2) **2
    BM = MM/2.0 - B2
    PCO=PCO2
    PCO2=B2/TK1*(0.50/TK2-SQRT(BB+B2/TK2)+BM)/(0.50/TK2-SQ
   1RT (BB+B2/TK2) - BM)
    B2=MM*XCO2-PCO2*HCO2
    PHS=0.0
    GO TO 933
204 FK1 = (KW*GAMA**2) / (KIC*KI*HH2S*AA*ALPHA)
    FK2 = (GAMA**2) / (KM*(AA*ALPHA) **2)
    FK3 = (AA*KW*KM) / (KI*KIY*HCO2)
    FFK=MM-Z-A1-B2
    IF (FFK) 953, 953, 954
953 FFK=MM/50.0
954 F1=PH2S-FK1*A1* (A1+B2) /FFK
    NEW VALUES OF PCO2, PH2S AND Z ARE NOW OBTAINED USING
    MODIFIED NEWTON-RAPHSON METHOD
    DD(1) = 1.0 + FK1 * (FFK * (2.0 * A1 + B2) + A1 * (A1 + B2)) * HH2S/FFK * * 2
    PH2S=PHS-F1/DD(1)
    A1=MM*XH2S-HH2S*PH2S
    FFK=MM-Z-A1-B2
    IF (FFK) 955, 955, 956
955 FFK=MM/50.0
956 F2=PCO2-FK2*Z*(A1+B2)/FFK**2
    DD(2) = 1.0 + FK2 + Z + HCO2 + (FFK + 2 + 2.0 + FFK + (A1 + B2)) / FFK + 4
    PCO2 = PCO - F2/DD(2)
    B2=MM*XCO2-HCO2*PCO2
    FFK=MM-Z-A1-B2
    IF (FFK) 957, 957, 958
957 FFK=MM/50.0
958 DD (3) = 1.0 + FK3 * (FFK + B2 - Z)
525 F3 = Z - FK3 * (B2 - Z) * FFK
    Z=ZZ-F3/DD(3)
    IF (Z) 505, 505, 506
```

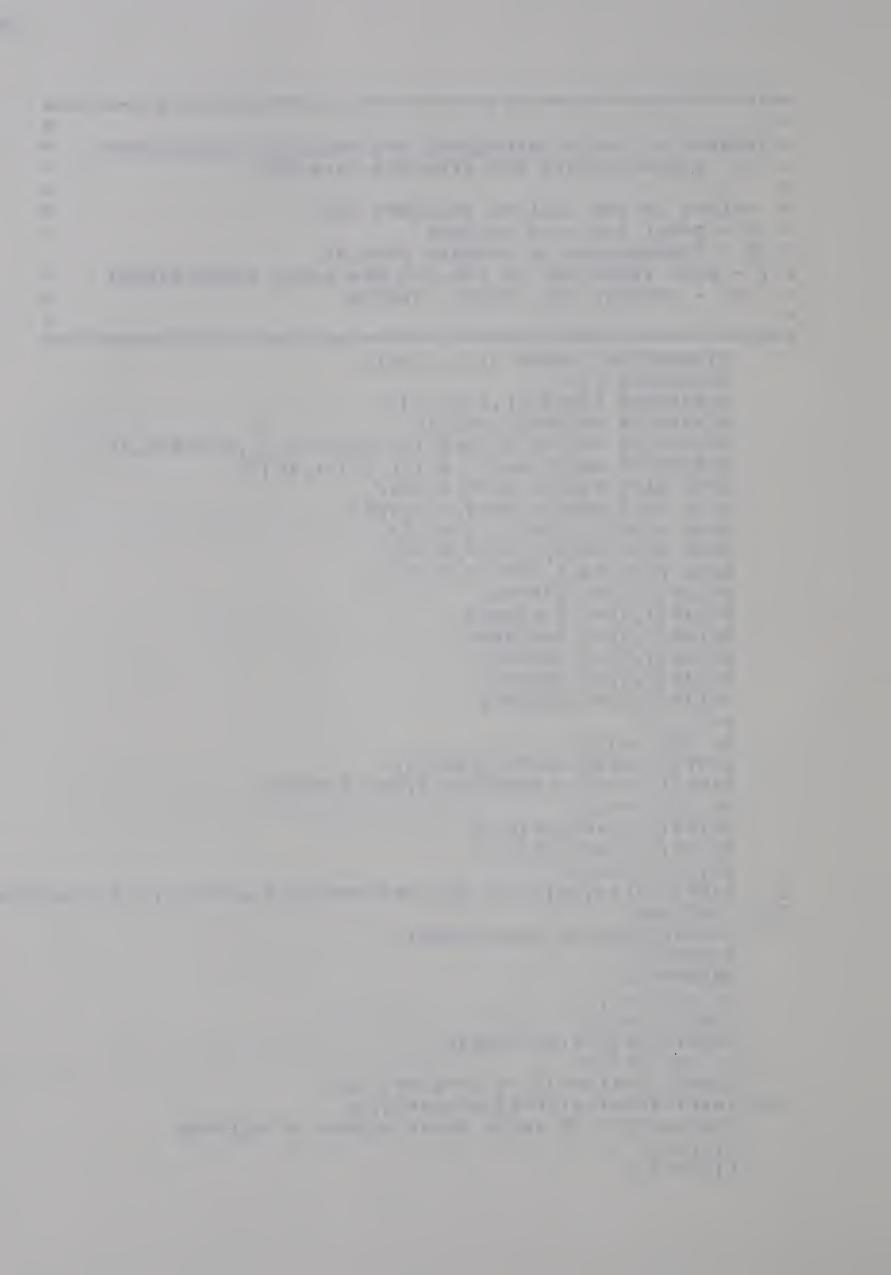
C



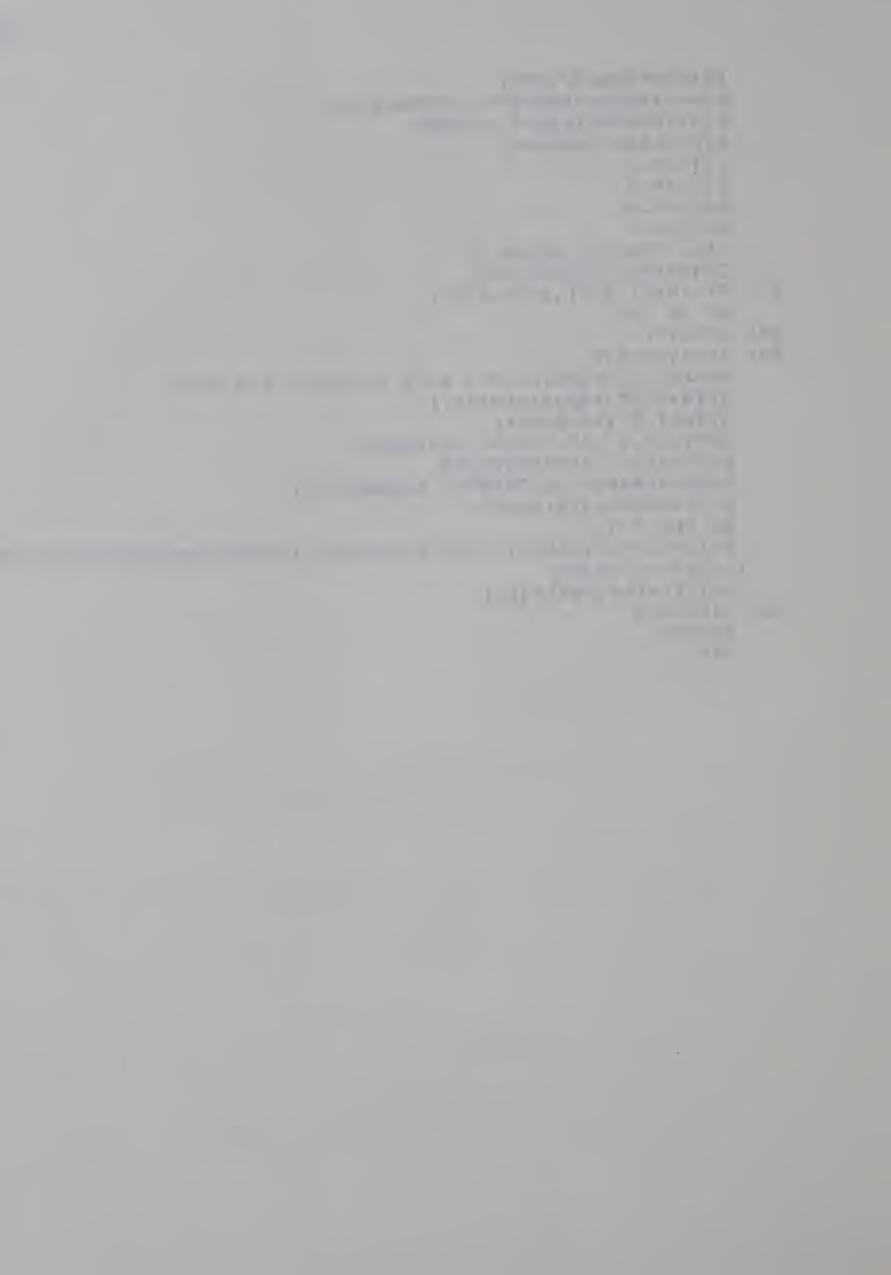
```
505 ZZ = 2.0 * ZZ
      GO TO 525
  506 \text{ IF } ((XCO2+XH2S)-0.2)833,833,934
  934 DHL=ALOG (ALPHA) /2.303+8.65-0.2150E04/T
      PH20=EXP(2.303*DHL)
      P=PH2S+PCO2+PH2O
      PP=P/51.70
      IF (PP-50.0) 933, 935, 935
  935 Y (1) = PH2S/P
      Y(2) = PCO2/P
      Y(3) = PH2O/P
      TRT = (T-273.16) *1.8 + 492.0
     CALL FUGCF (PP, TRT, Y, PHI)
      PH2S=PH2S/PHI(1)
      PCO2=PCO2/PHI(2)
      GO TO 933
  833 PPH=PH2S* (1.0-EXP(-XH2S*0.01)+2.0*EXP(-(0.06/XH2S))+EX
     1P(-0.05/(XCO2+XH2S*1.0)))*(1.0-0.00009/(XH2S**2))*(1.0
     2+(XCO2**2)/(2.5*XH2S))
      PH2S=PPH
      PPC = PCO2*(1.0-EXP(-XCO2*0.01)+2.0*EXP(-(0.07/XCO2))+EX
     1P(-0.05/(XCO2*0.2+XH2S)))*(1.0-0.002/XH2S)*(1.0-0.004/
     2XCO2) * (1.0 + XH2S * * 2 / (1.5 * XCO2))
      PCO2=PPC
      CHECKING OF CORRECTED VALUES
C
  933 IF (ABS ((PH2S-PHS) /PH2S*100.0) -5.0) 14,19,19
      IF (ABS ((PCO2-PCO)/PCO2*100.0)-1.0) 16,19,19
  16
      IF (ABS ((Z-ZZ)/Z*100.0)-5.0) 69, 19, 19
  19
      PHS=PH2S
      PCO=PCO2
      ZZ = Z
      IF (KL-11) 40,40,405
  405 WRITE (6, 406)
  406 FORMAT (//, 15x, 'NO CONVERGENCE AFTER 11 ITERATIONS' //,
     110x, 'THE LAST ESTIMATES WERE AS FOLLOWS :',//)
      WRITE (6,100) XCO2, XH2S, Z, PCO2, PH2S
      GO TO 108
  69
      WRITE (6,400) AA, ALPHA
  400 FORMAT (//, 2X, 'AA=', F7.4, //, 2X, 'ALPHA=', F7.4)
      WRITE (6,77) KL
      FORMAT (//, 2X, 'NO. OF ITERATIONS FOR CONVERGENCE TO PAR
     1TIAL PRESSURES= ', 13)
      PH2S=PH2S/51.7
      PCO2=PCO2/51.7
      WRITE (6, 100) XCO2, XH2S, Z, PCO2, PH2S
  100 FORMAT (//,9X,'XCO2',13X,'XH2S',10X,'RNHCOO(-)',6X,
     1'CO2 PARTIAL PRESS.',4X,'H2S PARTIAL PRESS.',//,2X,5E16.5,/
  108 CONTINUE
      CALL EXIT
      END
```



```
*********************************
 *
 * SUBROUTINE FUGCF CALCULATES THE FUGACITY COEFFICIENTS
    OF CARBON-DIOXIDE AND HYDROGEN-SULPHIDE
                                                              *
                                                              *
 \star
                                                              *
 *
    VALUES IN THE CALLING SEQUENCE ARE .
 *
    P - TOTAL PRESSURE IN PSIA
    T - TEMPERATURE IN DEGREES RANKINE
 * Y - MOLE FRACTIONS OF H2S, CO2 AND WATER RESPECTIVELY
    PHI - INITIAL FUG. COEFF. VECTOR
                                                              *
 ***************************
      SUBROUTINE FUGCF (P,T,Y,PHI)
      DIMENSION Y (3)
      DIMENSION AIRKV (3), A (4), Z (3)
      DIMENSION PHILN (3), PHI (3)
      DIMENSION ARKV (3,3), BRKV (3), PCIJV (3,3), TCIJV (3,3)
      DIMENSION GA(3), GB(3), PC(3), TC(3), VC(3)
      DATA GA/0.4340,0.4470,0.421/
      DATA GB/0.0882,0.0911,0.08368/
      DATA TC/672.7,240.0,1165.6/
      DATA VC/1.5606,2.3408,0.90/
      DATA PC/1306.0, 1071.0, 3208.0/
      PCIJV(1,2) = 0.5741E03
      PCIJV(1,3) = 0.21615E04
      PCIJV(2,3) = 0.10825E04
      TCIJV(1,2) = 0.3697E03
      TCIJV(1,3) = 0.8855E03
      TCIJV(2,3) = 0.5289E03
      R = 10.73
      DO 200 I=1,3
      BRKV(I) = GB(I) *R*TC(I) /PC(I)
      ARKV(I,I) = GA(I) *R**2*TC(I) **2.5/PC(I)
      DO 200 J=1.3
      PCIJV(J,I) = PCIJV(I,J)
      TCIJV(J,I) = TCIJV(I,J)
      IF(I-J)2,200,2
      ARKV(I,J) = ((GA(I) + GA(J)) *R**2*TCIJV(I,J) **2.5)/(2.0*PCIJV(I
  200 CONTINUE
C
      CALCULATION OF AMRKV, BRMKV
      AMRKV=0.0
      BMRKV=0.0
      DO 120 I=1.3
      AIRKV(I) = 0.0
      BMRKV = BMRKV + Y(I) * BRKV(I)
      DO 120 J=1,3
      AIRKV(I) = AIRKV(I) + Y(J) * ARKV(I, J)
  120 AMRKV = AMRKV + Y(I) * Y(J) * ARKV(I,J)
      CALCULATION OF VAPOR MOLAR VOLUME OF MIXTURE
      A(1) = 1.0
      A(2) = -1.0
```



```
PBRT = P * BMRKV/(R * T)
       ABRT = AMRKV/(BMRKV*10.73*T**1.5)
       A (3) = PBRT*(ABRT-1.0-PBRT)
      A(4) = -ABRT*PBRT**2
       Z(1) = 0.0
       Z(2) = 0.0
       Z(3) = 0.0
       MTYPE=-1
       CALL CUBEQ (A, MTYPE, Z)
       IF (MTYPE) 130,140,140
  130 ZV = AMAX1(Z(1), Z(2), Z(3))
       GO TO 150
  140 \text{ ZV} = \text{Z}(1)
  150 VV = ZV * R * T/P
C
       FUGACITY COEFFICIENTS WITH MODIFIED R-K EQN.
       QVVB=ALOG (VV/(VV-BMRKV))
       Q1VB=1.0/(VV-BMRKV)
       Q2RTB=2.0/(10.73*T**1.5*BMRKV)
       QVBV=ALOG((VV+BMRKV)/VV)
       QARTB=AMRKV/(10.73*T**1.5*BMRKV**2)
       QBVB=BMRKV/(VV+BMRKV)
       DO 160 I=1,3
       PHILN (I) = QVVB+BRKV (I) *Q1VB-AIRKV (I) *Q2RTB*QVBV+BRKV (I) *QART
     1-QBVB)-ALOG(ZV)
      PHI(I) = EXP(PHILN(I))
  160 CONTINUE
       RETURN
       END
```



\* \* \* \* \* SUBROUTINE AMAX1 FINDS THE MAX. Z VALUE \* \* FUNCTION AMAX1 (RR, SS, UU) AMAX1=RR IF(AMAX1-SS)2,3,32 AMAX1=SS 3 IF (AMAX1-UU) 4,5,5 4 AMAX1=UU 5 RETURN END

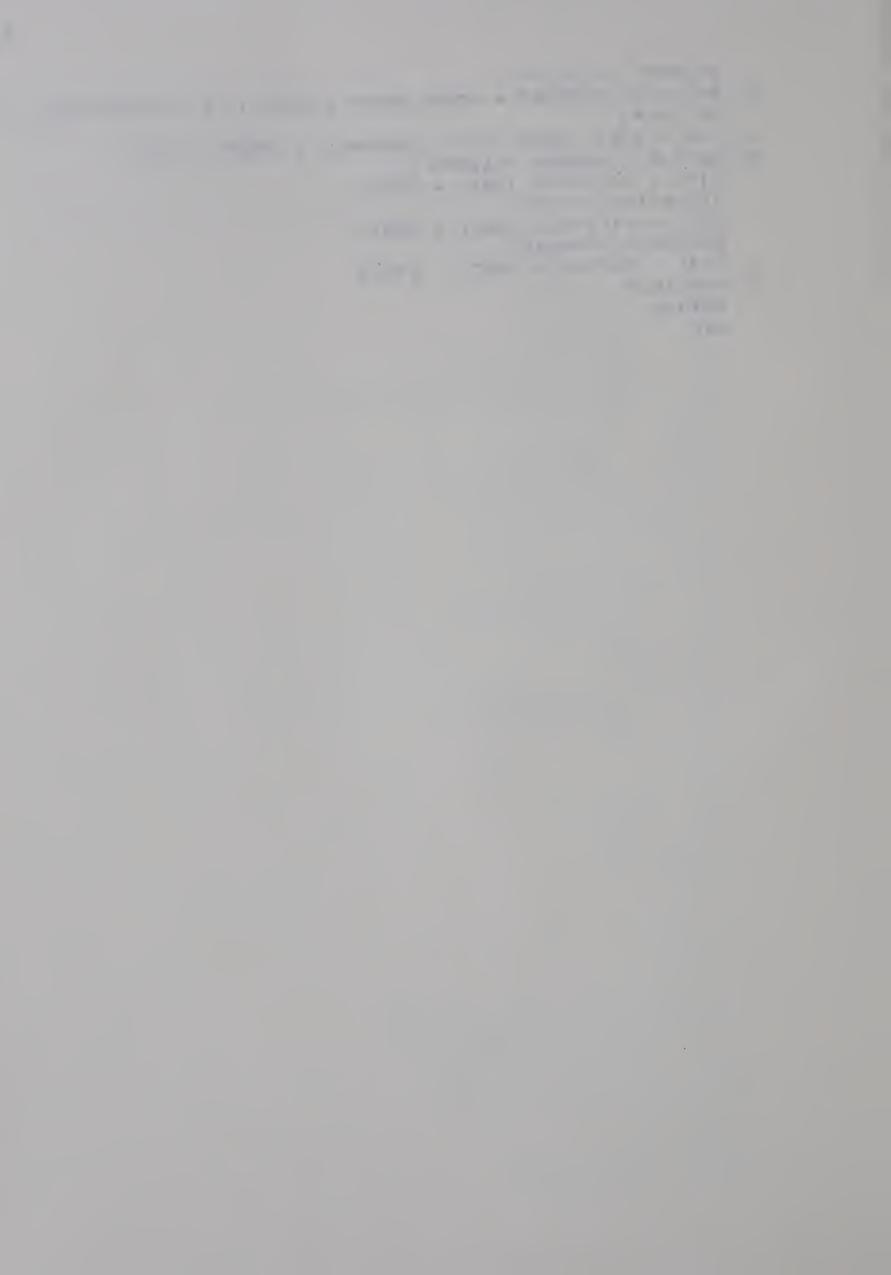


```
*****************************
 *
*
                                                          *
   THIS SUBROUTINE SOLVES CUBIC REDLICH-KWONG EQUATION
   FOR COMPRESSIBILITY FACTORS
 SUBROUTINE CUBEQ (A, MTYPE, Z)
     DIMENSION B (3), A (4), Z (3)
C
     B(1) = A(2)/A(1)
     B10V3 = B(1)/3.0
     B(2) = A(3)/A(1)
     B(3) = A(4)/A(1)
     ALF = B(2) - B(1) *B10V3
     BET = 2.0*B10V3**3 - B(2)*B10V3 + B(3)
     BETOV = BET/2.0
     ALFOV = ALF/3.0
     CUAOV = ALFOV **3
     SQBOV = BETOV **2
     DEL = SOBOV + CUAOV
     IF (DEL) 40,20,30
  20 \text{ MTYPE} = 0
     GAM = SQRT (-ALFOV)
     IF (BET) 22,22,21
  21 Z(1) = -2.0*GAM -B10V3
     Z(2) = GAM - B10V3
     Z(3) = Z(2)
     GO TO 50
  22 Z(1) = 2.0*GAM - B10V3
     Z(2) = -GAM - B10V3
     Z(3) = Z(2)
     GO TO 50
  30 \text{ MTYPE} = 1
     EPS = SQRT (DEL)
     TAU = -BETOV
     RCU=TAU+EPS
     SC U=TAU-EPS
     SIR=1.0
     SIS=1.0
     IF (RCU) 31,32,32
  31 SIR=-1.0
  32 IF (SCU) 33,34,34
  33 SIS=-1.0
  34 R=SIR*(SIR*RCU) **0.33333333
     S=SIS* (SIS*SCU) **0.33333333
     Z(1) = R + S - B10V3
     Z(2) = -(R+S)/2.0 * B10V3
     Z(3) = 0.86602540*(R-S)
     GO TO 50
  40 \text{ MTYPE} = -1
     QUOT = SQBOV /CUAOV
```

ROOT = SQRT (-QUOT)



```
IF (BET) 42,41,41
41 PEI = (1.5707963 + ATAN (ROOT / SQRT (1.0 - ROOT**2))) / 3.
GO TO 43
42 PEI = ATAN (SQRT (1.0 - ROOT**2) / ROOT) / 3.0
43 FACT = 2.0*SQRT (-ALFOV)
   Z(1) = FACT*COS (PEI) - B10V3
   PEI=PEI+2.0943951
   Z(2) = FACT*COS (PEI) - B10V3
   PEI=PEI+2.0943951
   Z(3) = FACT*COS (PEI) - B10V3
50 CONTINUE
   RETURN
   END
```



## APPENDIX G

EMPIRICAL CORRECTION FACTORS FOR MODIFIED KLYAMER ET AL. MODEL.



CORRECTED GAMA FUNCTIONS WHEN XCO2+XH2S IS >0.20

(1) FOR MEA

GAMA=0.399117-0.338402E-02\*MU+0.324219E00\*EXP(-MU)+0.1 15\*(1.0-(0.21/(XCO2+XH2S))\*\*0.95)+((XCO2+XH2S-0.4)/(1.0 2+EXP(-(7.2-MM))))\*(1.1-EXP(-(374.0-T)/100.0))

- (2) FOR DEA
- (I) WHEN ONLY ONE ACID GAS IS PRESENT

GAMA=0.36640-0.15975E-01\*MU+0.344379E00\*EXP(-MU)+(0.10 10\*(1.0-(0.21/(XCO2+XH2S))\*\*0.90)+0.1\*((XCO2+XH2S-0.05) 2/(XH2S+XCO2))\*(1.05-EXP(-(374.0-T)/100.0)))\*(1.05-EXP( 3-(5.22-MM)/10.0))

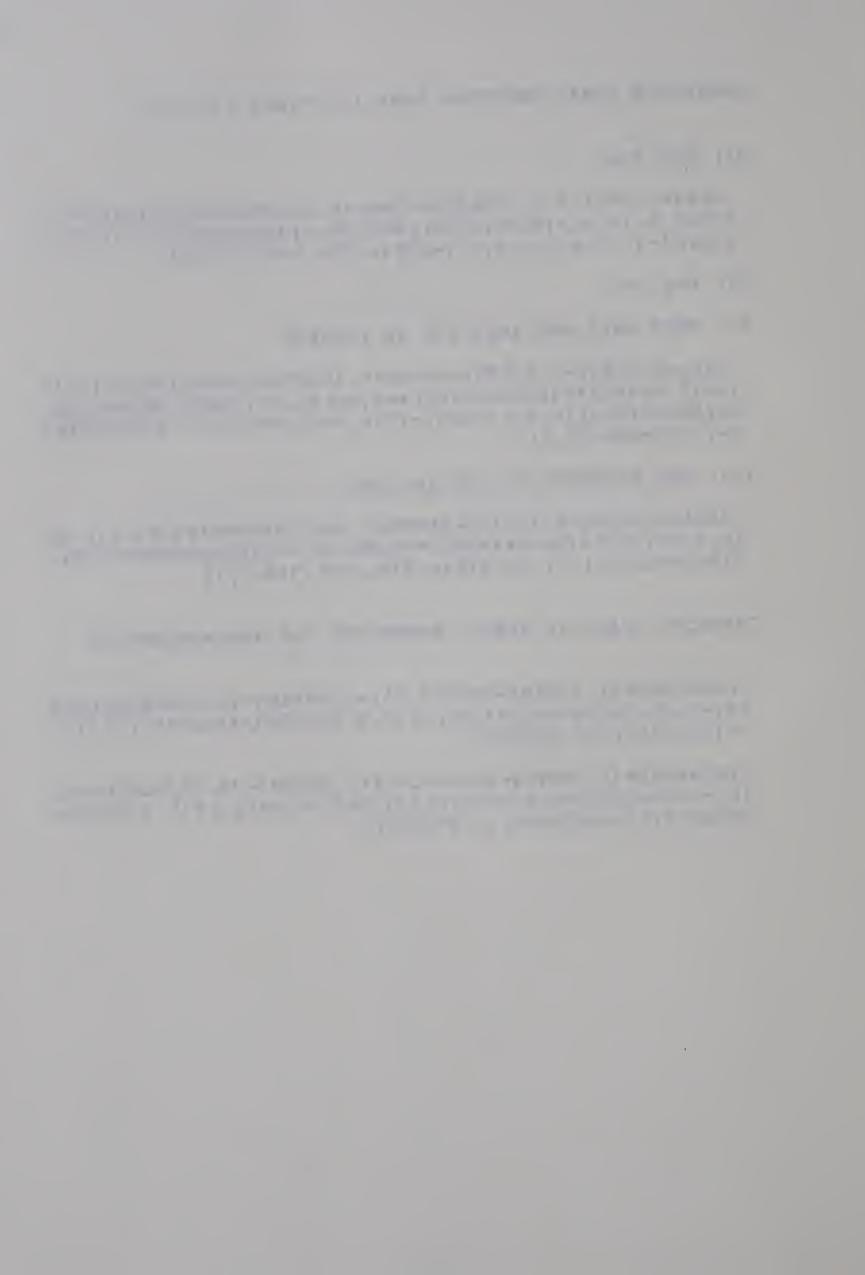
(II) FOR MIXTURES OF H2S AND CO2

GAMA=0.36640-0.15975E-01\*MU+0.344379E00\*EXP(-MU)+(0.10 1\*(1.0-(0.21/(XCO2+XH2S))\*\*0.90)+0.5\*((XCO2+XH2S-0.30)/2(XH2S+XCO2))\*(1.05-EXP(-(374.0-T)/100.0)))

CORRECTED PARTIAL PRESS. FUNCTIONS FOR XCO2+XH2S<0.20

PPH=PH2S\* (1.0-EXP(-XH2S\*0.01)+2.0\*EXP(-(0.06/XH2S))+EX 1P(-0.05/(XCO2+XH2S\*1.0)))\*(1.0-0.00009/(XH2S\*\*2))\*(1.0 2+(XCO2\*\*2)/(2.5\*XH2S))

PPC=PCO2\* (1.0-EXP(-XCO2\*0.01)+2.0\*EXP(-(0.07/XCO2))+EX 1P(-0.05/(XCO2\*0.2+XH2S)))\*(1.0-0.002/XH2S)\*(1.0-0.004/ 2XCO2)\*(1.0+XH2S\*\*2/(1.5\*XCO2))



## APPENDIX H

POLYNOMIAL APPROXIMATIONS OF

$$K_{1Y}$$
,  $K_{2Y}$ ,  $H_{CO_2}$ ,  $\gamma$  and  $\alpha$ 



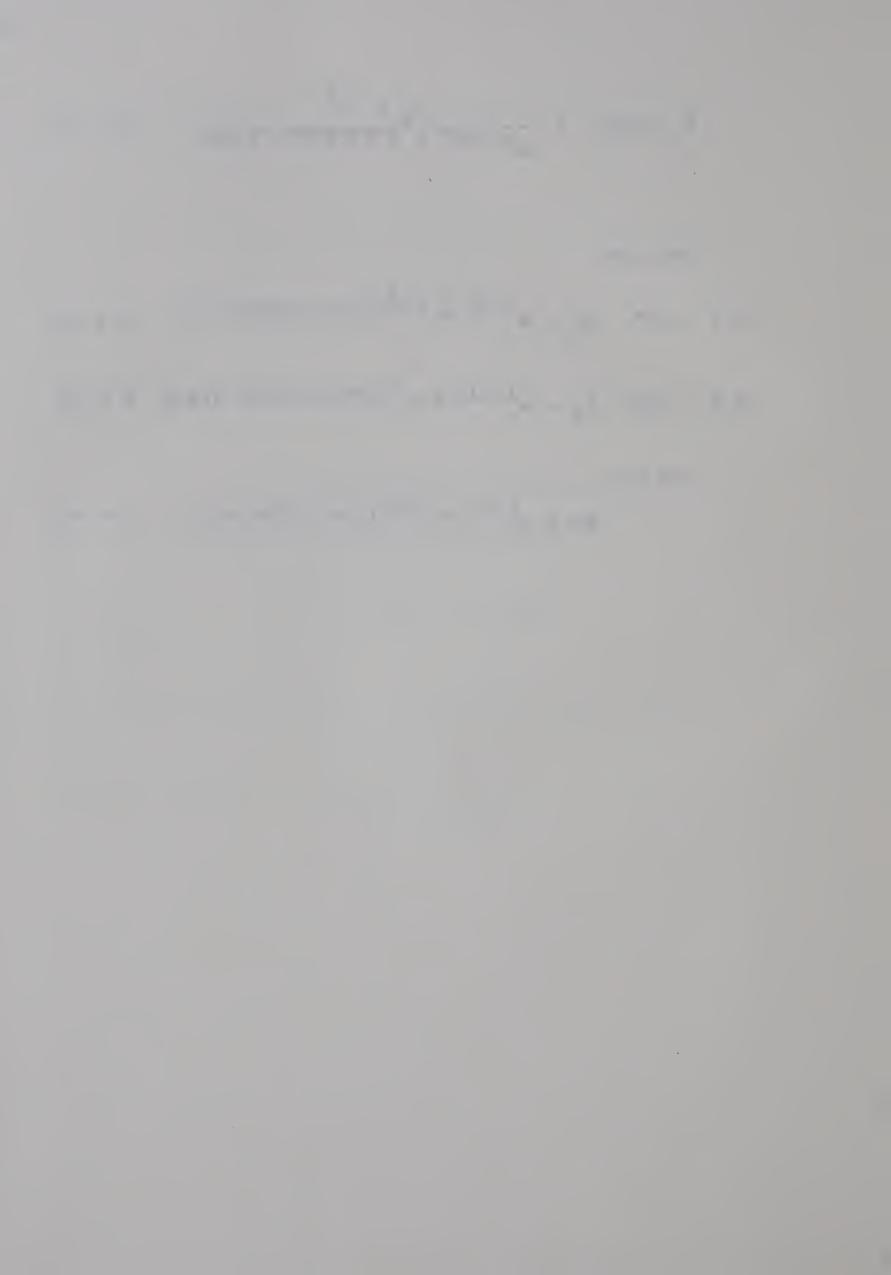
$$k_i \text{ (DEA)} = \frac{K_w \times 10^8}{e^{-1.609 + 0.0415 (T - 37.8)}}$$
  $T = ^{\circ}C$ 

For MEA

If T < 65° 
$$K_{\rm m} = e^{4.58 \times 10^3 (1/T-0.00295)-1.5}$$
  $T = °K$ 

If T > 65°C 
$$K_m = e^{4.742 \times 10^3 (1/T-0.0025)-3.634}$$
 T = °K

$$Km = e^{3.66} \times 10^{3} (1/T-0.0026)-4.0$$
  $T = °K$ 

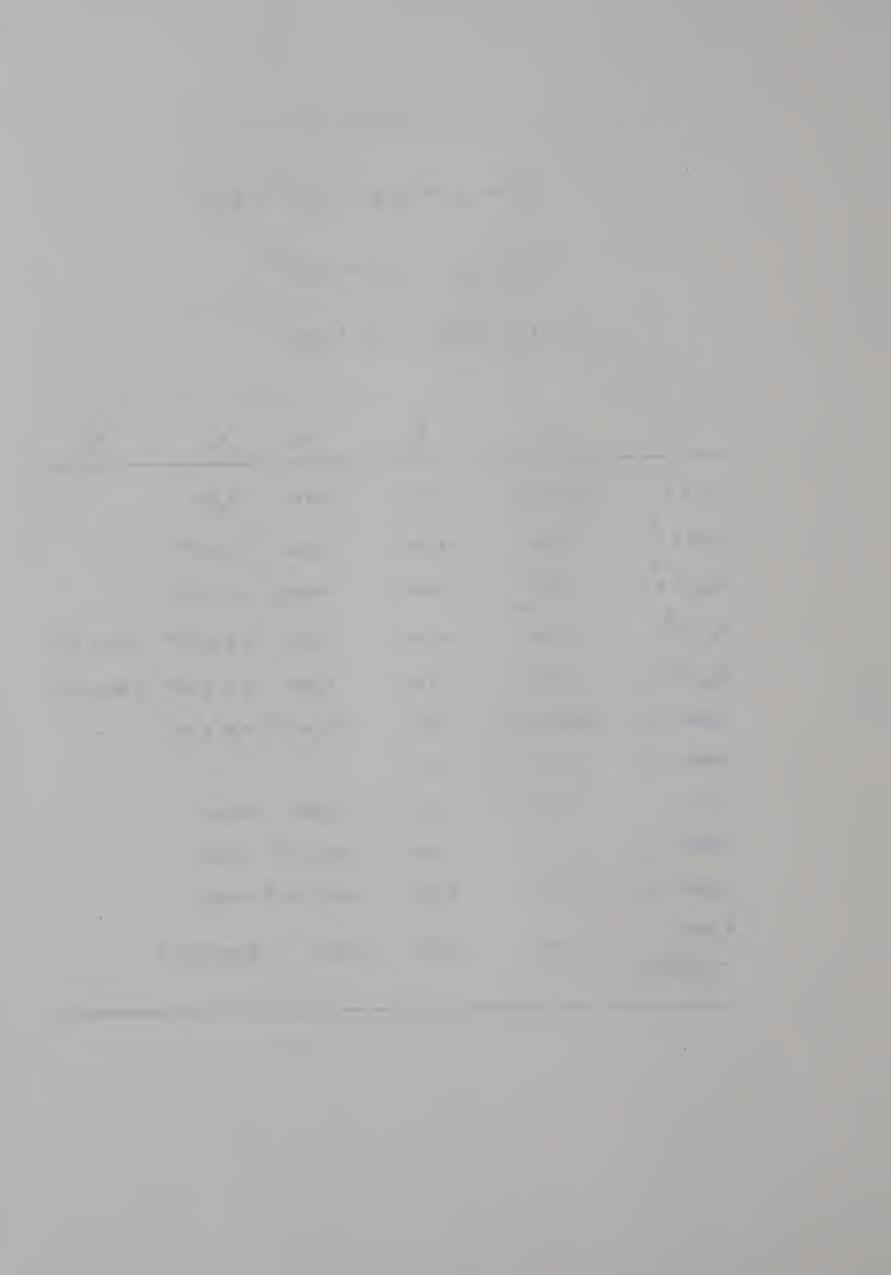


$$Y_1 = a_0 + a_1x + a_2x^2 + a_3x^2$$

$$Y_2 = a_0 + a_1x + a_2e^{-x}$$

$$Y_3 = a_0/x + a_1 + a_2x$$

Yi	×	a <sub>o</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>
$K_{1Y} = e^{Y_1}$	1/T (K <sup>-1</sup> )	8.724	-1.833	0.3375	••
$H_{H_2}S = e^{Y_1}$	т (°К)	-4.508	0.0453	-6 x 10 <sup>-5</sup>	-
$^{\mathrm{H}}\mathrm{CO}_{2} = \mathrm{e}^{\mathrm{Y}_{1}}$	T (°K)	-2.4835	0.03612	4.4 x 10 <sup>-5</sup>	-
$K_w = e^{Y_1}$	T (°F)	-0.7564	0.0279	7.0 x 10 <sup>-5</sup>	7.47 x 10 <sup>-8</sup>
$K_{1C} = e^{Y_1}$	T (°F)	0.1108	0.0167	6.85 x 10 <sup>-5</sup>	1.07 x 10 <sup>-7</sup>
$a(DEA) = Y_1$	m (molality)	0.8575	1.258 x 10 <sup>-2</sup>	4.42 x 10 <sup>-3</sup>	-
$a (MEA) = Y_1$	m ≥ 0.4	0.8727	-		von.
$\gamma = Y_2$	μ ≤ 0.1	0.9623	-1.996	-0.068	vole.
$\gamma (MEA) = Y_2$	μ > 0.1	0.3991	$-3.384 \times 10^{-3}$	0.3242	-
$\gamma$ (DEA) = $Y_2$	μ > 0.1	0.3664	1.598 x 10 <sup>-2</sup>	0.3444	-
$K_{i} \text{ (MEA)}$ $= \frac{K_{w}}{e^{2.303 \text{ Y}_{3}}}$	T (°K)	-2677.9	-0.6169	4.277 x 10 <sup>-4</sup>	





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